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Photoluminescent Properties of p-GaAs/Electrolyte Interface. Evidence for Bandedge Shift during Photoelectrochemical Hydrogen Evolution Reaction

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When the potential of p-GaAs electrode was pulsed from -1.0 V (vs. Ag/AgCl) to a potential more positive than ca. -0.35 V, PL intensity increased sharply and the PL spectrum broadened but the intensity declined and the spectrum shrank gradually with time. These results are explained by the bandedge shift during the photoelectrochemical hydrogen evolution.

In the study of photoelectrochemical reactions at semiconductor electrodes, the knowledge of energy levels of the bands are very important.[1] Mott-Schottky plots are often employed to determine the flat band potential and, thereby, the bandedge position.[2] The shift of the bandedge energy level by illumination has been reported recently.[3] Luminescence measurements are known to be useful to probe the potential distribution at semiconductor/electrolyte interfaces and the energy levels of electrochemical reaction intermediates and surface states.[4] We have applied the photoluminescence (PL) and electroluminescence (EL) measurements to study the hydrogen evolution reaction at n- and p-GaAs and reported the energy levels of adsorbed hydrogen atom on p-GaAs[5] and the accumulation layer formation at n-GaAs.[6] In this communication, we used PL measurements to probe the potential distribution at p-GaAs/0.5 M H_2SO_4 solution (1 M=1 mol dm^{-3}) and found the bandedge shift during the photoelectrochemical hydrogen evolution reaction.

The potential dependence of PL intensity was correlated qualitatively with the passage of photocurrent in early studies[7] but recently more quantitative treatment was applied to photoelectrochemical systems by Ellis and his coworkers.[8] Their treatment is based on a "dead layer" model.[9] According to the model, there exists a non-emissive zone, dead layer, because electron-hole pairs formed within this region are swept apart more rapidly than the radiative decay due to the electric field. Thus, the PL intensity at a certain potential under reverse bias is given by[12]

$$I = I_{fb} \exp\{ -(\alpha + \beta) W \} \quad (1)$$

where I_{fb} is the PL intensity at the flat band potential at which no dead layer exists, W is the dead layer width at the given potential and α and β are the ab-

sorption coefficient at the wavelength of excitation light and that of emitted light at the measuring wavelength, respectively. As mentioned before, Kelly and Memming reported that the Mott-Schottky plot of p-GaAs shifted in negative direction by 200 mV under illumination at potentials more negative than -0.3 V but approached to that in dark at more positive potentials.[3a) They attributed this shift to a change of potential drop in the Helmholtz layer, resulting from electron trapping at the surface state. If this model is correct, the bandedge shift in positive potential direction with time is expected when the electrode potential is pulsed from relatively negative potential to the potential more positive than -0.3 V. Correspondingly, the dead layer width becomes thicker and the PL intensity decreases with time as expected from Eq. 1.

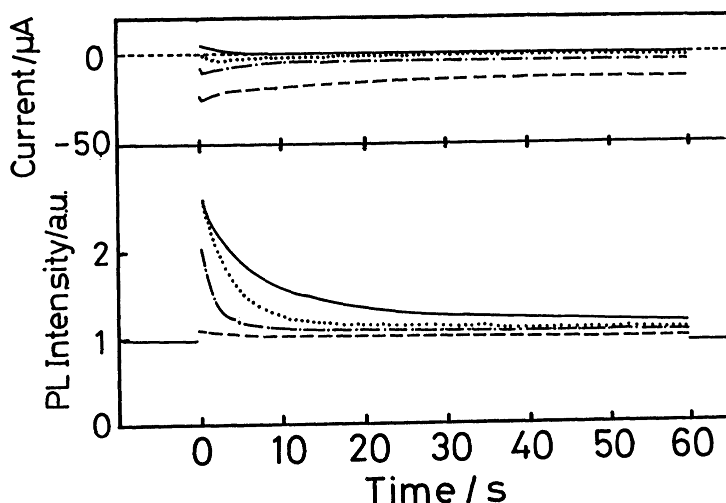

Fig. 1. Transient responses of current and PL intensity when potential was pulsed from -1.0 V to Vp. Vp: -0.35 V (– – – –), -0.2 V (—·—·-), -0.1 V (··········) and 0.0 V (———).

To prove this bandedge shift, transient behaviors of current and PL intensity at p-GaAs (NEC Corp., Zn doped: 2×10^{19} cm^{-3}) were measured by pulsing the potential from -1.0 V to a more positive potential, Vp, and are shown in Fig. 1. When the potential was pulsed to Vp,[11)] the less cathodic photocurrent and the higher PL intensity were observed. If Vp was more positive than ca. -0.35 V, the PL intensity reached maximum just after the application of the potential pulse and decreased gradually with time to a steady value. If the potential was pulsed back to -1.0 V and again pulsed to Vp, the same transient behavior was observed. Thus, the results in Fig. 1 suggest that while the electrode potential was kept constant, the potential drop within the semiconduc-

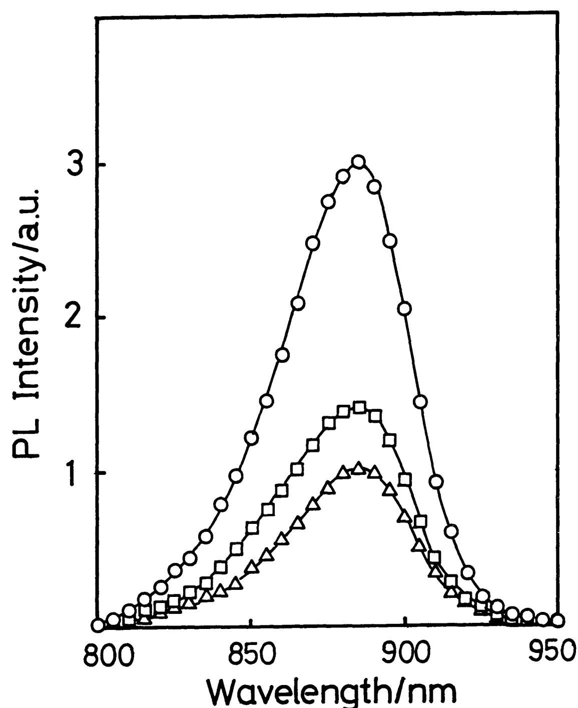

Fig. 2. PL spectra just before (—△—) and just after (—○—) the potential pulse to -0.15 V and in steady state at -0.15 V (—□—).

tor changed with time so that the dead layer width also changed with time and support the bandedge shift proposed by Kelly and Memming.

To confirm the change of the dead layer thickness with time, the PL spectra were measured at -1.0 V just before the potential pulse to -0.15 V was applied, that just after the pulse was applied, i.e., at -0.15 V, and that in steady state at -0.15 V[12] and are shown in Fig. 2. Although the peak position was same in all cases at 885 nm, suggesting that this emission was caused by a band to band transition or by a transition from the conduction band to the acceptor level which is located just above the valence band,[13] the spectrum just after the pulse was applied had larger FWHM (=52 nm), broadened particularly at shorter wavelength region, than those at -1.0 V (FWHM=47 nm) and in steady state at -0.15 V (FWHM=48 nm). Since the absorption coefficient, β, is larger at shorter wavelength ($\beta<8\times10^2$ for $\lambda>880$ nm and $\beta>8\times10^3$ for $\lambda<870$ nm[14]), the higher energy portion of the emission band is more strongly absorbed for the PL emitted deeper in the bulk and the broadening of the spectrum at shorter wavelength portion should be attributed to the PL emitted from the nearsurface region of the semiconductor. Thus, the result in Fig. 2 means that the PL was emitted from the region closer to the semiconductor surface just after the application of the potential pulse than before that, but emitting zone became deeper with time. This result supports the conclusion drawn from the transient behavior of the PL intensity (Fig. 1).

A band model is proposed in Fig. 3 to explain the results of Kelly and Memming and of the present study. When the electrode potential is -1.0 V under illumination, the valence bandedge is relatively negative because the flat band potential, V^{*}_{fb}, is relatively negative. When the electrode potential is pulsed to Vp which is more positive than -1.0 V, the band bending becomes smaller and the dead layer width, W^{*}_{Vp}, becomes thinner than that at -1.0 V, allowing the emission from an inner part of $W^{*}_{-1.0}$. Therefore, the PL intensity increases and the PL spectrum becomes broader. When Vp is more positive than -0.35 V, the nature of the electrode surface changes with time due to the oxidation of adsorbed and absorbed

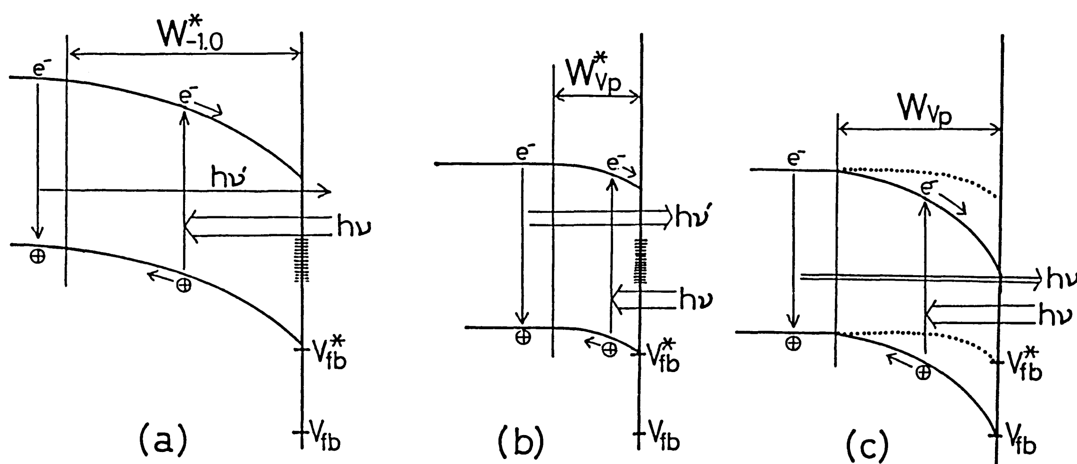

Fig. 3. The band diagrams of p-GaAs/electrolyte interface (a) at -1.0 V, (b) just after the potential pulse to Vp and (c) in steady state at Vp.

hydrogen formed during photoelectrochemical hydrogen evolution at -1.0 V and/or oxide formation,[15] resulting in changes in a degree of the charge localization in the surface states which causes the potential distribution change at semiconductor/electrolyte interface, i.e., bandedge shift. As the bandedge shifts in positive potential direction with time, the band bending becomes larger and the dead layer width becomes thicker with time. Accordingly, the PL intensity decreases and the PL spectrum becomes narrower especially in shorter wavelength portion with time since the PL is again emitted only from the deeper portion of the semiconductor.

More quantitative analysis will be published elsewhere.

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11) Light from a 25 mW He-Ne laser (NEC Corp., GLG5700) was exposed on the electrode surface as excitation light. The emitted light was detected by a photomultiplier tube (Hamamatsu Photonics. Co. Ltd., R406 and R636) through a monochromator (Ritsu Oyo Kogaku Co. Ltd., MC-25NP) and the PMT signal was amplified by using a fast response amplifier (NF Electronics. Co. Ltd., LI-57A, 1 MHz, gain=100). The current and the PL intensity were recorded by a personal computer (NEC Corp., PC-8801mkII) via 8ch. 12bit A/D converter.
12) The PL intensity was monitored at the wavelength of every 5 nm from 800 nm to 950 nm and the resposes similar to that in Fig. 1 was obtaied at each wavelength. The PL spectra at a given time were constructed by using the data thus obtained. The personal computer was used to record the data and to control the monochromator by sending pulsed signals to a monochromator driver unit.
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