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Photoluminescence Proof of the Increase of Surface Recombination Velocity at p-GaAs Electrode by Pt Treatment

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Photoluminescence measurements with excitation light of several wavelengths were employed to investigate the effect of noble metal treatment on hydrogen evolution reaction at semiconductor electrode. It was demonstrated that surface recombination velocity was increased by Pt treatment leading to higher dark current and lower photocurrent.

Photoluminescence (PL) measurements of semiconductors in solution can probe the potential and charge distribution at semiconductor/electrolyte interfaces as well as surface recombination velocity and, therefore, provide useful information of the mechanism of photoelectrochemical reactions.[1-5)]

Hydrogen evolution reaction (HER) at p-type semiconductor electrodes is one of the most important photoelectrochemical reactions at semiconductor electrodes. Usually, the large overpotential with respect to the flatband potential (FBP) is required for HER at p-type III-V semiconductors such as p-GaAs, GaP and InP.[6-8)] The overpotential may be decreased by modifying the semiconductor surface with various metals.[9-11)] We found that, while p-InP modified by Co-Mo synergetic catalyst shows higher efficiency,[12)] Ru^{3+} treatment increases HER rate at p-GaAs in the dark but reduces the photocurrent. These results show that the Ru^{3+} treatment introduces surface states which act as recombination centers.[13)]

In this paper, we applied PL measurements with excitation light of several wavelengths to investigate the effect of Pt treatment on HER at p-GaAs electrode and demonstrated that the surface recombination velocity was increased by Pt treatment leading to higher dark current and lower photocurrent.

A Zn doped (4.66×10^{18} cm^{-3}) p-GaAs single crystal obtained from Morgan Semiconductor was used in this study. An ohmic contact was obtained by In-Zn alloy. The electrode surface was etched in HNO_3-HCl (1:1) before each experiment. Pt treatment of the electrode was carried out by dipping the electrode for 15 s in

20 mM H_2PtCl_6 (1 M=1 mol dm^{-3}).[14] The electrolyte solution was prepared by using reagent grade NaOH and water purified by a Milli-Q water purification system. An ordinary two-compartment, three-electrode cell with a Pyrex window was used for the measurements. A counter and a reference electrode were a Pt foil and a Ag/AgCl electrode, respectively. The electrode potential was controlled by using a potentiostat and a function generator. A block diagram of the luminescence measurements is shown in Fig. 1. A 500W Xe lamp was used as an excitation light source. Light from the Xe lamp was passed through an appropriate interference filter and a light chopper and was illuminated onto the electrode surface. The emitted light from the electrode was passed through a monochromator and was detected by a photomultiplier tube (Hamamatsu Photonics, R636). PL intensity was determined by using a photon counter (NF Electronics, PC-545A). The counting duration was 0.3 ms. The counting was started 0.05 ms after the light chopper was opened or closed to avoid an error due to diffused reflection. A personal computer (NEC, PC 8801 mkII) was used to control the photon counter by sending a pulsed signal and for the data acquisition.

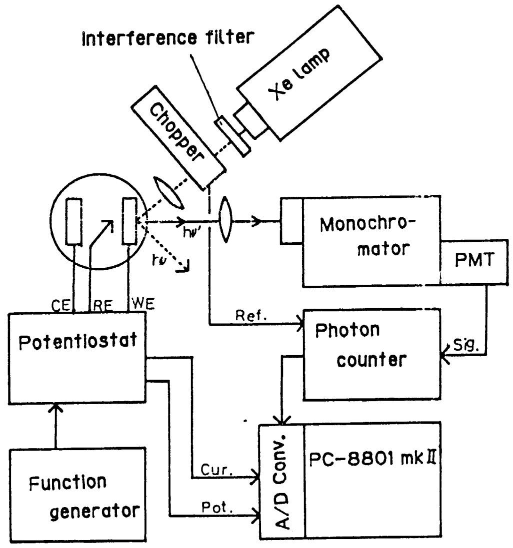

Fig. 1. Block diagram for electrochemical and luminescence measurements.

Although, as the excitation wavelength became shorter, the intensity of the emitted light from the electrode became smaller, the peak positions of the spectra

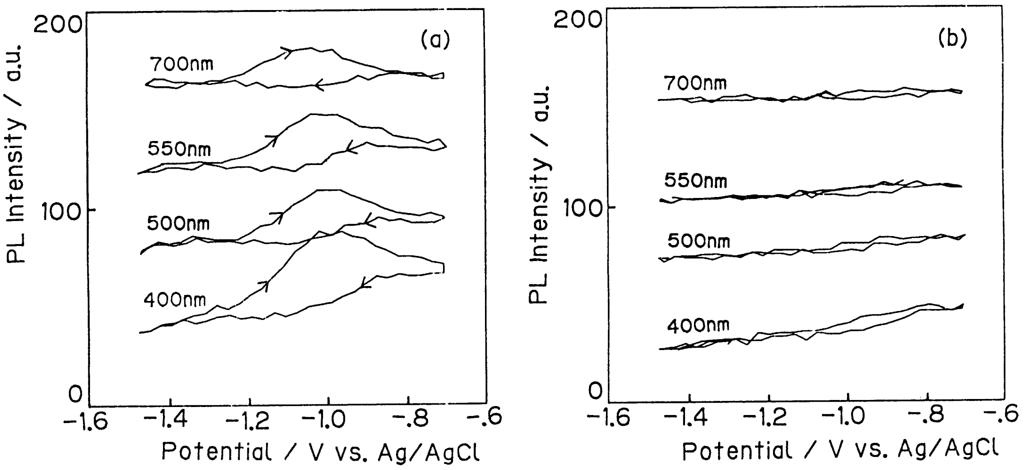

Fig. 2. PL intensity-potential relations of (a) etched and (b) Pt treated p-GaAs electrodes in 1 M NaOH measured by using several excitation wavelengths.

were constant in all cases at 870 nm. The potential dependence of PL intensities were, therefore, monitored at the peak wavelength. Figure 2 shows the potential dependence of the etched and Pt treated p-GaAs electrode in 1M NaOH for various excitation wavelengths. At both electrodes, the potential dependence of PL intensities increased as the excitation wavelengths became shorter. Hysteresis was observed in PL intensity-potential relations at etched p-GaAs but almost reversible relations were obtained at the Pt treated electrode. These results suggest that, while surface nature of etched p-GaAs changes during potential sweep, that of Pt treated electrode was relatively constant.

The space charge layer width and surface recombination velocity can be determined by analyzing the results obtained above as follows. According to Mettler, the PL intensity is given by[15)]

$$I_{PL} = k \frac{\alpha_e L}{(\alpha_e L)^2 - 1} \exp\{-(\alpha_e + \alpha_p)W\}\left[\frac{S_{rv} + \alpha_e L}{(S_{rv} + 1)(\alpha_e L + 1)} - \frac{1}{(\alpha_e + \alpha_p)L}\right] \qquad (1)$$

where k is a constant containing the integral quantum efficiency and geometrical factors, L is the diffusion length of the minority carrier, α_e and α_p are the absorption coefficients at the wavelength of excitation light and emitted light, respectively, W is a space charge layer width, and S_{rv} is a reduced surface recombination velocity defined as

$$S_{rv} = S_v(\tau/L) \qquad (2)$$

where S_v is a virtual surface recombination velocity and τ is the lifetime of the minority carrier. W and S_{rv} were determined by fitting the PL intensity obtained experimentally at various excitation wavelength, i.e., penetration depth, $1/\alpha_e$, to Eq.1. The fitting was carried out by using Statistical Analysis System (SAS) at Hokkaido University Computing Center. Literature values are used for absorption coefficients at given wavelengths[16)] and L was assumed as 4 µm.[17)] The justification of this value for L was provided by Johnson et al.[17)] Figure 3 shows the experimental results of the PL intensity of etched p-GaAs at -0.7V vs. Ag/AgCl (o) and the best fit (solid line) based on Eq.1. W and S_{rv} are determined as 4.0×10^{-7} cm and 14.6, respectively, in this case. The potential dependence of S_{rv} at etched and Pt treated p-GaAs are shown in Fig. 4. The current density

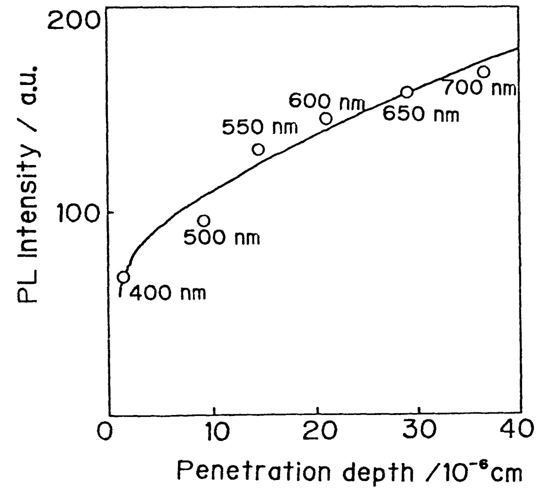

Fig. 3. Penetration depth dependence of PL intensity of etched p-GaAs electrode at -0.7 V vs. Ag/AgCl.

seemed to have little effect on S_{rv} as current was almost zero at -0.7 V and several mA cm^{-2} at -1.4 V. The values of S_{rv} at Pt treated surface were larger than that at etched surface. We have reported that Ru^{3+} treatment introduces not only a catalytically active surface but also surface states that act as recombination centers.[13] The increase of S_{rv} observed in the present study confirms the introduction of recombination centers by noble metal treatment. We showed in a separate paper[18] that the density of surface states introduced by Pt treatment is as high as 2.45×10^{13} cm^{-2}.

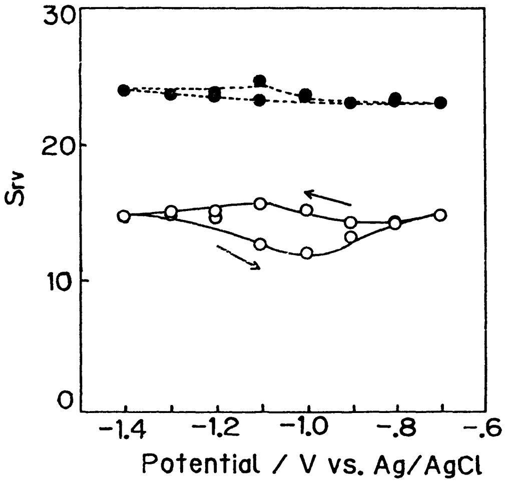

Fig. 4. The potential dependence of S_{rv} at etched (-o-) and Pt treated (---●---) p-GaAs electrodes in 1M NaOH.

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