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Electroluminescent Properties of *n*-GaAs in Peroxodisulfate Solutions. Transient Behavior and Carrier Concentration Effect on Emission Spectra

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Electroluminescence (EL) due to band-to-band transition was observed for *n*-GaAs in solutions containing peroxodisulfate ions. Digital simulation shows that the observed transient current and EL intensity stimulated by negative potential pulses can be explained by assuming that the surface concentration of $S_2O_8^{2-}$ was zero during potential pulses and that the EL intensity was proportional to the surface concentration of $SO_4^{\cdot-}$ (generated by the one-electron reduction of $S_2O_8^{2-}$). Surface composition change seems to be the main reason for the relation between the potential and EL intensity. A hydrogen evolution reaction reduces the EL efficiency at relatively negative potentials. Although the potential and time had no observed effect on the shape of the EL spectra, the carrier concentration affected the peak position and the full width at half maximum (FWHM) of the EL spectra. For greater carrier concentrations, the wavelength of the EL peak became shorter and the FWHM became larger. These results agree with those reported regarding solid-state luminescence and can be explained by the filling of the conduction band states by electrons (Burnstein-Moss shift).

The luminescent properties of semiconductors in solutions have proved to be useful in understanding the mechanism of electrochemical reactions at semiconductor electrodes.[1—10)] Photoluminescence (PL) measurements are often used to determine the quantum efficiency of photoelectrochemical reactions[11—13)] and electroluminescence (EL) measurements are used to probe the intermediates of reactions and the surface states of semiconductors.[14—18)]

Gallium arsenide (GaAs) has been one of the most frequently studied semiconductors and its luminescent properties at p/n and semiconductor/metal junctions have become well known.[19—25)] The luminescent properties of GaAs in solution, however, have been studied less. Recently, Hobson and Ellis thoroughly studied the photoluminescent properties of *n*-GaAs in a solution containing Te^{2-}/Te_2^{2-}.[26)] Only a few reports are available involving the electroluminescence properties of GaAs.[27—30)]

In this paper, we describe the transient behavior of the current and the EL intensity of *n*-GaAs electrodes in solutions containing $S_2O_8^{2-}$ and the effect of carrier concentration on the EL spectra.

Experimental

Materials. Four types of *n* -GaAs single crystals with different carrier concentrations were used in the present study. Their properties are summarized in Table 1. Ohmic contacts to the crystals were obtained using an In-Ga alloy. The procedure for mounting the electrodes was similar to one reported before.[31)] The electrode surface was etched in HNO_3-HCl (1:1) before each experiment. Reagent-grade NaOH and $K_2S_2O_8$, and water purified using a Milli-Q water purification system (Millipore Corp.) were used to prepare electrolyte solutions.

Electrochemical and Luminescent Measurements. The potential of the electrode was controlled with a potentiostat (Hokuto Denko, HA-301) with respect to an Ag/AgCl reference electrode. A large Pt foil, which surrounded a GaAs working electrode, was used as a counter electrode. The EL intensity was monitored with a photomultiplier (Hamamatsu TV Co. Ltd., R406) having a response similar to S-1. A programmable function generator (Hokuto Denko, HB-105) and a wave-memory unit (NF Electronic Co. Ltd., WM-811 with an 8-bit resolution) were used to study the transient behavior of the EL intensity and current. Both the function generator and the wave-memory unit were controlled by a personal computer (Nippon Electronic Co. Ltd., PC-8801) *via* a GP-IB interface and a PIO interface with TTL signals, respectively. After each measurement, data were transferred to the computer and, to improve the signal-to-noise ratio, the data were averaged 2—64 times. The averaged data were then transferred to and stored on a floppy disc. The time sequence for the transient behavior measurements is shown in Fig. 1(a).

Time-resolved EL spectra were obtained by pulsing the potential between −0.5 V and −3.65 V, following the time sequence shown in Fig. 1(b). In this case, the computer was used to provide potential pulses *via* a 12-bit D/A convertor, to collect the photomultiplier (PMT) response which was amplified by a fast-response amplifier (NF Electronic Co. Ltd., LI-75A, 1 MHz, gain=100) *via* a 12-bit D/A convertor every 10 msec and to control a monochromator (Ritsu Oyo Kogaku Co. Ltd., MC-20N, having a grating with 1200 grooves/mm blazed at 0.75 μm). After the EL intensity was measured and averaged at one wavelength, the monochromator was driven to make measurements at a new wavelength. After all the measurements were completed, the EL data were trans-

TABLE 1. PROPERTIES OF *n*-GaAs SINGLE CRYSTALS

Sample	Face	Dopant	Donor density/cm^{-3}	Specific Resistance/Ω·cm	Mobility/cm^2·V^{-1}·s^{-1}
1	(100)	Si	0.84×10^{18}	0.0033	2235
2	(100)	Si	2.6×10^{18}	0.0015	1656
3	(100)	Si	$4.2-8.0\times10^{18}$	0.0007—0.0008	1171—1882
4	(100)	Te	0.96×10^{18}	0.0024	2712

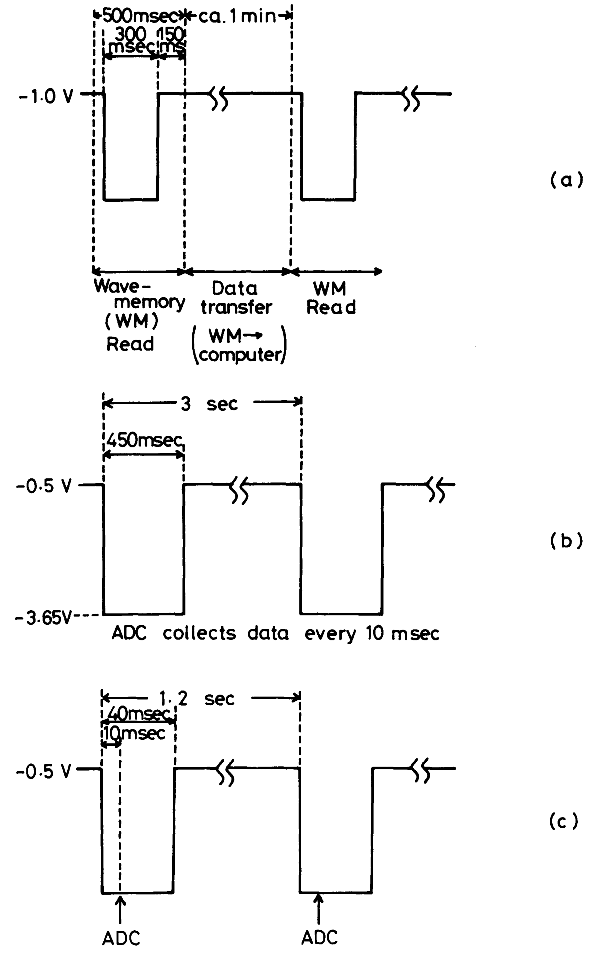

Fig. 1. Time sequence for the measurements of (a) transient behavior, (b) time resolved EL spectra, and (c) potential dependence of EL spectra.

ferred to and stored on a floppy disc.

Similar arrangements were employed to study the potential dependence of the EL spectra. The time sequence for this type measurement is shown in Fig. 1(c). The potential was pulsed between −0.5 V and a given potential. The resulting PMT response was observed at a given wavelength 10 msec after the potential step, amplified by the LI-75A amplifier, monitored by a 12-bit A/D convertor and stored in the computer. After measurements at a given potential were completed, measurements at new potentials were carried out. Measurements were repeated at 2.5 or 5 nm intervals. After all the measurements were completed, the EL data were transferred to and stored on a floppy disc.

Digital simulation was carried out using the computer and calculated results were plotted on an X-Y plotter (RY 11Z, Rika Denki Co. Ltd.).

Results

The Transient behavior and Potential Dependence of Current and EL Intensity. Typical EL-i-t relations of *n*-GaAs (sample No.4) in a solution containing 5 M NaOH (1 M=1 mol dm^{-3}) and 0.10 M $K_2S_2O_8$ for potential pulses of 300 msec are shown in Fig. 2. The electrode potential was kept at −1.0 V for about 1 min before each potential pulse. As the pulse was made more negative, the maximum EL intensity became greater and the maximum cathodic current became larger. The potential dependence of the EL intensity is, in general, not so simple. The EL intensity and the current at 50, 100, 200, and 295 msec after the cathodic potential pulse was applied are plotted against the pulsed potential (Fig. 3). The EL intensity was made to increase by applying a more negative cathodic pulse, until *ca.* −1.9—−2.0 V. However, it decreased between −2.0 and −2.2 V and then increased again.

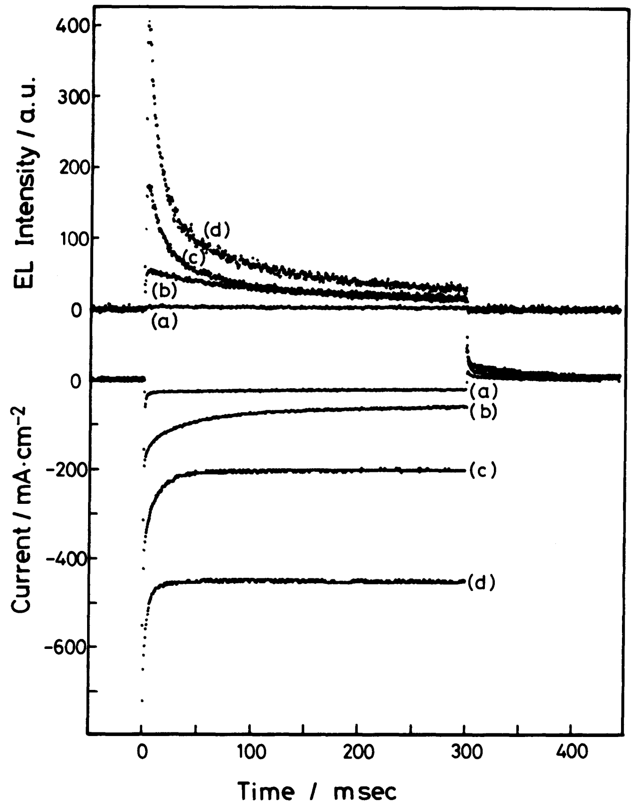

Fig. 2. EL-i-t relations of *n*-GaAs (Te doped, 0.96×10^{18} cm^{-3}) in a solution containing 5 M NaOH and 0.10 M $K_2S_2O_8$ for potential pulses from −1.0 V (1 min) to a given potential (300 msec). (a): −1.5 V, (b): −2.0 V, (c): −2.5 V, (d): −3.0 V.

EL Spectra. The EL Spectra of *n*-GaAs (sample No.4) in a solution containing 5 M NaOH and 0.15 M $K_2S_2O_8$ at 10, 30, 50, and 70 msec after a potential was pulsed from −0.5 V to −3.65 V are shown in Fig. 4(a). The EL peak appeared at 855 nm (1.45 eV), which is in good agreement with the band-gap energy of GaAs.[32] There seems to be no spectral change within this time domain, which is clearly seen in Fig. 4(b) where the EL spectra are normalized to the peak intensity of each spectrum.

To study the potential dependence of the EL spectra, only data 10 msec after the pulses were applied were obtained for four GaAs samples, since there was no spectral change during the potential pulse. Typical EL spectra are shown in Fig. 5(a). Normalized spectra are shown in Fig. 5(b). No potential effect on EL spectra was observed in any of the four samples.

The relation of carrier concentration on the EL spectra was also studied. Since no time or potential depen-

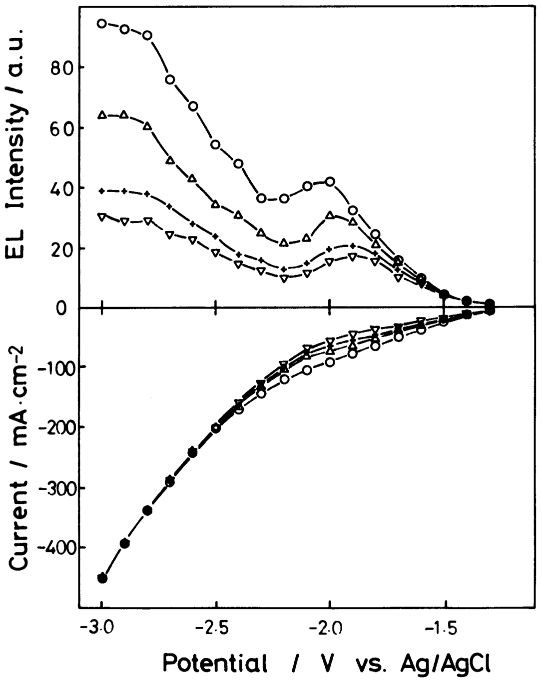

Fig. 3. Pulsed potential dependence of EL intensity and current at 50 (○), 100 (△), 200 (+), and 295 (▽) msec after potential was stepped from −1.0 V. Other experimental conditions are as same as those of Fig. 2.

dencies were observed, only the normalized EL spectra obtained 10 msec after the potential was pulsed from −0.5 V to −3.5 V are shown in Fig. 6. For higher carrier concentrations, the peak energy increased and the FWHM of the EL spectra became larger. It was rather difficult to study the effect of carrier concentration on EL intensity quantitatively because the surface area of the electrodes and the alignment varied from experiment to experiment. The effect of a dopant on spectral shape was negligible, as far as a comparison between Si and Te was concerned.

Although Pettinger *et al.* reported that sub-band emission is much stronger than band-edge emission for *n*-GaAs,[27] we observed only small, if any, sub-band emission. Because of the poor sensitivity of the PMT employed in this study at wavelengths longer than 1000 nm, it is not possible to quantitatively compare the intensity of the band-edge emission to that of the sub-band emission.

Discussion

It is well known that the EL of *n*-type semiconductors in solutions containing $S_2O_8^{2-}$ is predominanly caused by the following reactions[6]

$$S_2O_8^{2-} + e_c^- \longrightarrow SO_4^{\cdot-} + SO_4^{2-}, \tag{1}$$

$$SO_4^{\cdot-} \longrightarrow SO_4^{2-} + p_v^+. \tag{2}$$

Thus, $S_2O_8^{2-}$ is first reduced by electrons of the conduction band, e_c^-, producing $SO_4^{\cdot-}$ which is a strong oxidant to be able to inject holes into the valence band of semiconductors, p_v^+. A part of p_v^+ recombine radiatively with e_c^- either directly or *via* intermediate levels such as surface states, lattice defects or impurity states. The former process generates edge emission and the latter sub-band emission. As mentioned before, the energy of the major peak in the EL spectra of GaAs in this study coincides with the energy gap of GaAs, suggesting that the band-to-band transition is the dominant process in the generation of EL.

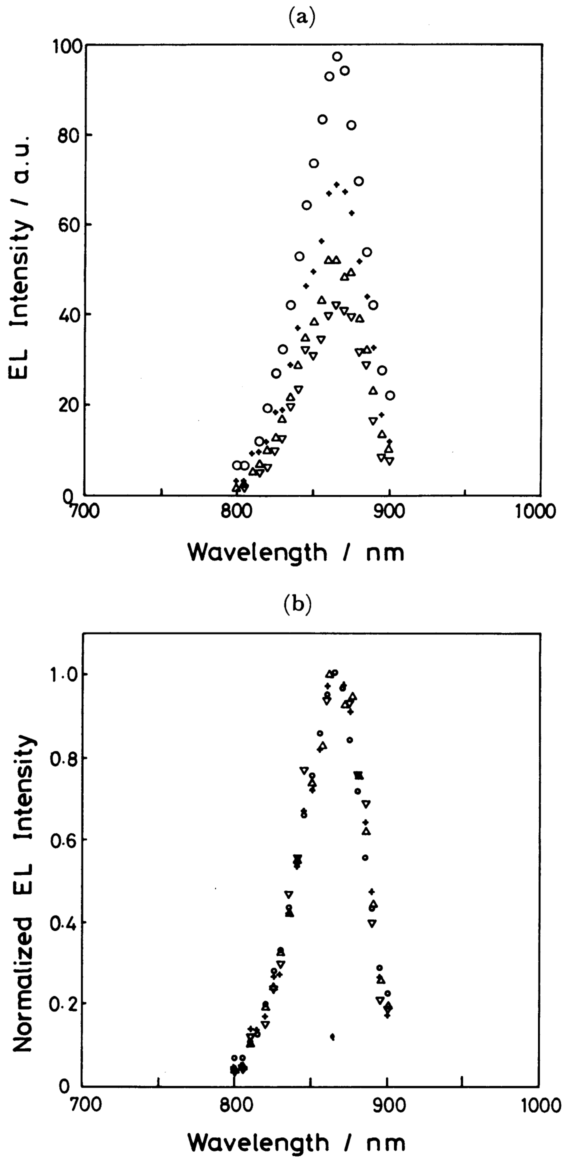

Fig. 4. EL spectra (a) and normalized EL spectra (b) of *n*-GaAs (Te doped, 0.96×10^{18} cm^{-3}) in a solution containing 5 M NaOH and 0.15 M $K_2S_2O_8$ at 10 (○), 30 (+), 50 (△), and 70 (▽) msec after potential was pulsed from −0.5 V to −3.65 V.

The transient behaviors of the EL of *n*-ZnO and of ZnS were studied by Yamase and Gerisher[5] and by Fan *et al.*[7], respectively, but that of *n*-GaAs is not available. The potential dependence of the transient behavior of EL and current is more clearly seen by studying the transient behavior of EL efficiency, which is the ratio of the EL intensity to current, as shown in Fig. 7. The S/N ratio at relatively positive potentials was low because of

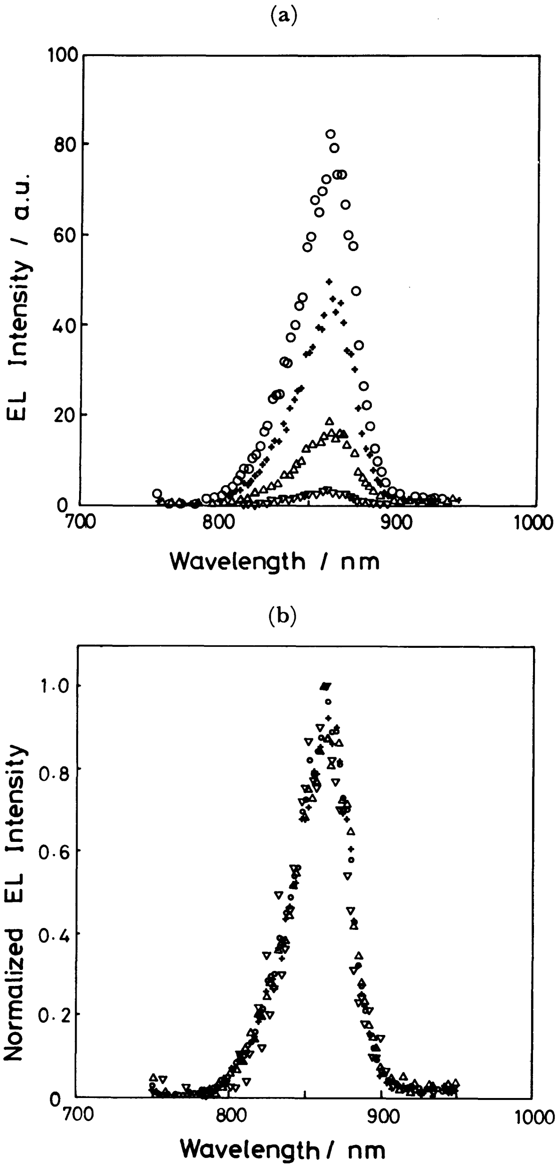

Fig. 5. EL spectra (a) and normalized EL spectra (b) of *n*-GaAs (Si doped, $0.84\times10^{18}\ \mathrm{cm}^{-3}$) in a solution containing 5 M NaOH and 0.15 M $K_2S_2O_8$ at 10 msec after potential was pulsed from −0.5 V to −2.5 V (▽), −3.0 (△), −3.5 (+), and −4.0 (○) V.

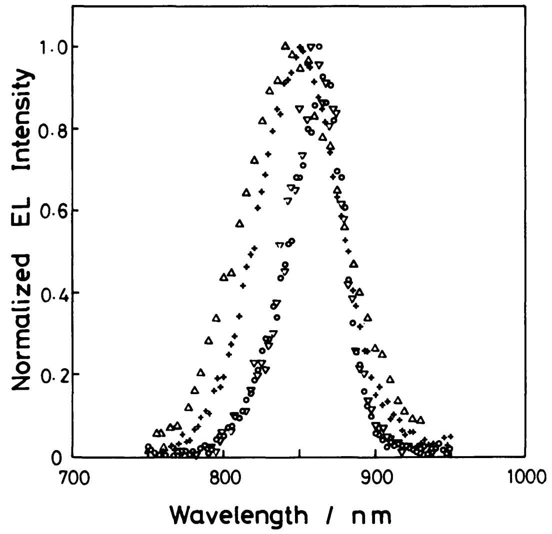

Fig. 6. Normalized EL spectra of *n*-GaAs in a solution containing 5 M NaOH and 0.15 M $K_2S_2O_8$ at 10 msec after potential was pulsed from −0.5 V to −3.5 V. ○: Si doped; $0.84\times10^{18}\ \mathrm{cm}^{-3}$, +: Si doped; $2.6\times10^{18}\ \mathrm{cm}^{-3}$, △: Si doped; $4.2-8.0\times10^{18}\ \mathrm{cm}^{-3}$, ▽: Te doped; $0.96\times10^{18}\ \mathrm{cm}^{-3}$.

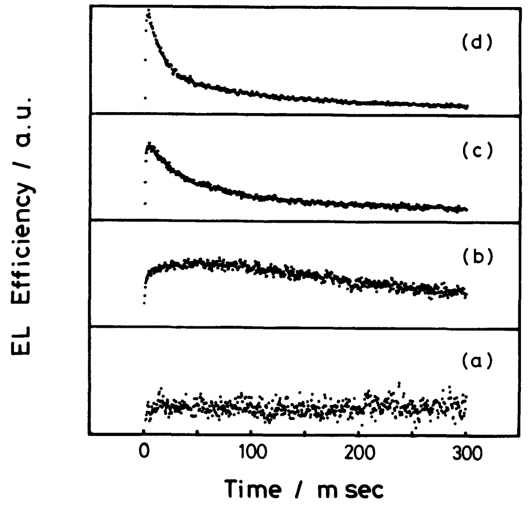

Fig. 7. Transient behavior of EL efficiency calculated from the data in Fig. 2.

the small values of EL intensity and current. It is, however, clear that while the efficiency was almost constant at −1.5 V, it gradually increased and then decreased with time at −2.0 V. A similar trend was observed at more negative potentials but the time to reach the maximum intensity was smaller at more negative potentials. The EL efficiency-potential relations for different time domains are shown in Fig. 8. There is a clear maximum in each relation around −2.2 V. Similar results were reported for *n*-GaAs in solutions containing several hole-injecting species,[30] for *n*-InP in dilute nitric acid[10] and for ZnO in a solution containing $S_2O_8^{2-}$.[5] Two reasons should be considered. One is the depletion of $S_2O_8^{2-}$ near the electrode surface and the other is a change in surface characteristics. At the beginning of the potential pulse, no $SO_4^{\cdot-}$ exists and, therefore, no EL is observed. $SO_4^{\cdot-}$ is generated by the reaction (1) and the EL intensity increases. However, $S_2O_8^{2-}$ is depleted at the surface and eventually $SO_4^{\cdot-}$ also decreases. Thus, the EL intensity decreases. This can be formulated, semiquantitatively, by assuming that the surface concentration of $S_2O_8^{2-}$ is zero during the potential pulse, *i.e.*, the rate of reaction (1) is controlled by diffusion of $S_2O_8^{2-}$, and EL intensity is proportional to $SO_4^{\cdot-}$ concentration. The surface concentration of $SO_4^{\cdot-}$, c_s, is given by solving

$$\frac{\mathrm{d}c_s}{\mathrm{d}t}=\frac{\sqrt{D}c^*}{\sqrt{\pi t}}-k_1c_s, \tag{3}$$

where D and c^* are the diffusion coefficient and bulk concentration of $S_2O_8^{2-}$, respectively, k_1 is the rate constant for reaction (2) and t is the time after potential is

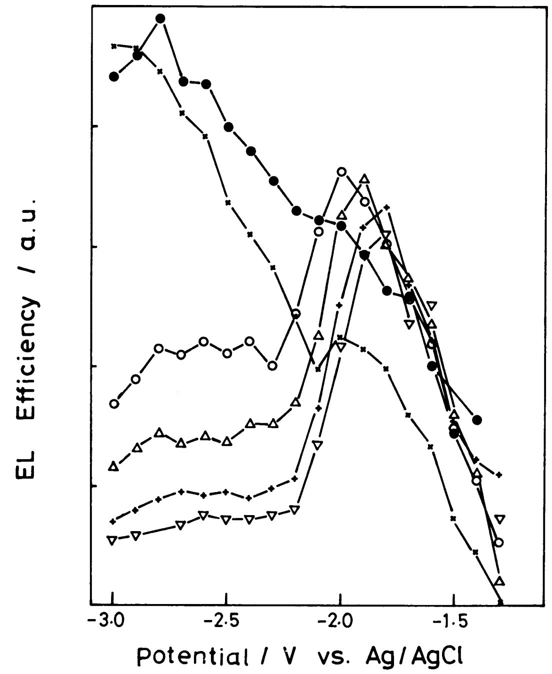

Fig. 8. Pulsed potential dependence of EL efficiency at 1 (▲), 10 (×), 50 (○), 100 (△), 200 (+), and 295 (▽) msec after potential was stepped from -1.0 V. Other experimental conditions are as same as those of Fig. 2.

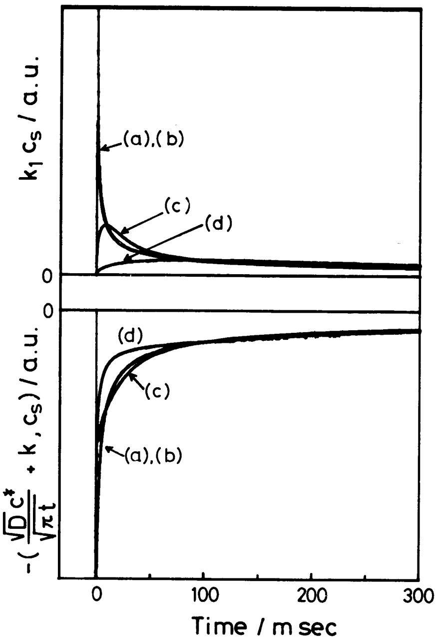

Fig. 9(a). Time dependence of $\left(-\frac{\sqrt{Dc^*}}{\sqrt{\pi t}}+k_1c_s\right)$ which is propotional to current and k_1c_s which is propotional to EL intensity.
$D=10^{-5}$ cm^2 s^{-1}. $c^*=10^{-3}$ M. $k_1=10000$ s^{-1} (a), 1000 s^{-1} (b), 100 s^{-1} (c), and 10 s^{-1} (d).

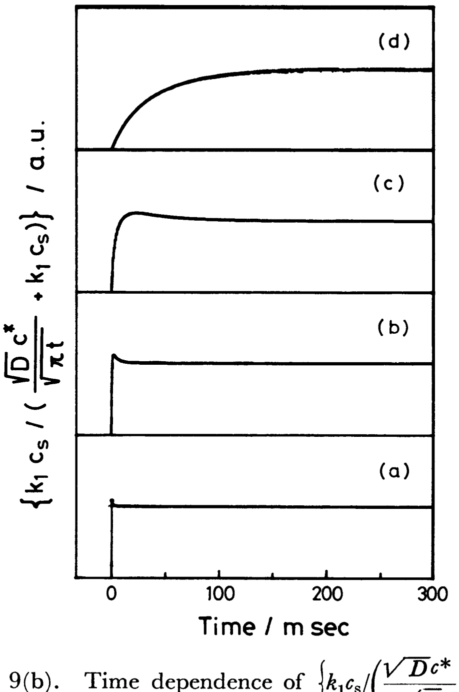

Fig. 9(b). Time dependence of $\left\{k_1c_s/\left(\frac{\sqrt{Dc^*}}{\sqrt{\pi t}}+k_1c_s\right)\right\}$ which is propotional to EL efficiency. Parameters for the calulation are as same as those of Fig. 9(a).

pulsed. The EL intensity, I_{EL}, is given by

$$I_{EL} = \eta k_1 c_s, \qquad (4)$$

where η is the EL efficiency. η should be determined by surface characteristics. To see if this simple model could explain the EL-t relations, Eq. 3 was solved using a digital-simulation technique. Figure 9(a) shows k_1c_s, which is proportional to I_{EL} if η is assumed to be constant, and $\frac{\sqrt{Dc^*}}{\sqrt{\pi t}}+k_1c_s$, which is proportional to the current due to reduction of both $S_2O_8^{2-}$ and $SO_4^{\bar{\cdot}}$, against time for several values of k_1. The time dependence of the relative EL efficiency, *i.e.*, $k_1c_s/(\frac{\sqrt{Dc^*}}{\sqrt{\pi t}}+k_1c_s)$, is shown in Fig. 9(b). The results in Fig. 9 prove that EL-i-t and EL efficiency-t relations can be explained by just considering a simple concentration profile change as a function of time. Of course, a hydrogen evolution reaction becomes a dominant process when $S_2O_8^{2-}$ is depleted, particularly at relatively negative potentials and its contribution to the EL efficiency should be taken into account in a more thorough examination.

Although the time dependence of the EL can be explained by just considering the depletion of $S_2O_8^{2-}$ (as shown above), the potential dependence of EL intensity and EL efficiency needs other explanations. When the potential was made more negative, band bending and the concentration of electrons in the conduction band near the surface became greater. Since the radiation recombination of electrons in the conduction band and holes in the valence band is more effective at a higher concentration of electrons in the conduction band and holes in the valence band,[21] the EL efficiency should be higher at more negative potentials. The EL-V and EL efficiency-V relations show that this is not so. Around -2.0 V, the EL starts to decrease after applying a more negative potential.

Decker *et al.* proposed that a compositional change in the semiconductor surface, which was suggested for GaAs by Gerischer and Mattes,[33] causes the EL quenching for GaAs in solutions containing various redox agents.[30] Thus, the present GaAs was also covered with an oxide layer at −1.0 V and the potential pulse to −2.1—−2.2 V introduced unsaturated surface states (dangling bonds) which acted as recombination centers and reduced radiation recombination. Thus, η in Eq. 4 first increases with a more negative polarization due to a larger band bending while the surface characteristics remain constant. However, η starts to decrease beyond *ca.* −2.0 V because of the introduction of the recombination centers. When the potential is pulsed in this region, a change in the surface composition is initiated. Since composition change needs some time, EL intensity (efficiency) is high even at this potential region just after the pulse is applied. When the potential becomes much more negative (*e.g.* −2.3 V), the surface states are restabilized by hydride formation and η, *i.e.*, EL intensity, again increases, although the EL efficiency measured later than 50 msec after the potential pulse is applied does not increase even at these potentials, because the hydrogen evolution reaction becomes dominant.

Although Bard *et al.* reported that the EL spectral shape of ZnS was affected by current (*i.e.*, potential) and time,[7] no such effect was observed in our experiment. This difference is reasonably understood since only the potential dependence on the band-edge emission spectra was investigated in the present study, while the EL observed at ZnS was the sub-band emission. There could be some effect in the sub-band emission region even in the present arrangement, but it was not detected clearly enough to be analysed.

The carrier concentration dependence of the cathode- and photo-luminescent spectra of GaAs have been measured using p/n and Schottky junctions, but no report on EL in a solution is available. The results in Fig. 6, *i.e.*, a blue shift of the peak energy and a widening of the peak at highly doped GaAs, are, however, in good agreement with the results reported for solid-state luminescence[22] and can be explained by the filling of the conduction band sates by electrons (Burnstein-Moss shift).[34] These results again confirm that the EL spectra obtained are due to band-edge emission and suggest that the EL study at a semiconductor/solution interface conveniently provides information on band-edge energy.

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