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# Enhancement of Electroluminescence at Porous Silicon/Electrolyte Interface

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An Electroluminescence (EL) of porous silicon in the electrolyte of $Na_2SO_4$ + $S_2O_8{}^{2-}$ at the cathodic bias was greatly enhanced as much as 30 times by adding $C_2H_5OH$. The dependence of EL spectra on cathodic bias potential was also detected similarly to as that without $C_2H_5OH$. The enhancement mechanism of EL was discussed considering with the current density dependence during EL emission in the electrolyte with and without $C_2H_5OH$.

An porous silicon formed by anodization of silicon in HF solution, has been widely interested due to its photoluminescence (PL) phenomenon.1,2) An electroluminescence (EL) of porous silicon was also reported not only in porous silicon/metal or ITO systems3-5) but also in porous silicon/electrolyte solution system.6-8) Visible EL can be produced from cathodically biased porous silicon in electrolyte containing a strong oxidizing agent, such as peroxodisulfate ion ($S_2O_8{}^{2-}$).7,8) The mechanism for the EL in this system is considered to be the same one for typical n-type semiconductor which is shown in Fig. 1 with following reactions from (1) to (3).9)

$$S_2O_8{}^{2-} + e^- \rightarrow SO_4{}^{2-} + SO_4{}^{\bullet -} \quad (1)$$

$$SO_4{}^{\bullet -} \rightarrow SO_4{}^{2-} + p^+ \quad (2)$$

$$e^- + p^+ \rightarrow h\nu \quad (3)$$

Interestingly, the EL spectra were reported to be influenced by the potential of cathodic bias; the peak of the spectra are known to shift toward shorter wavelength with an increase in cathodic

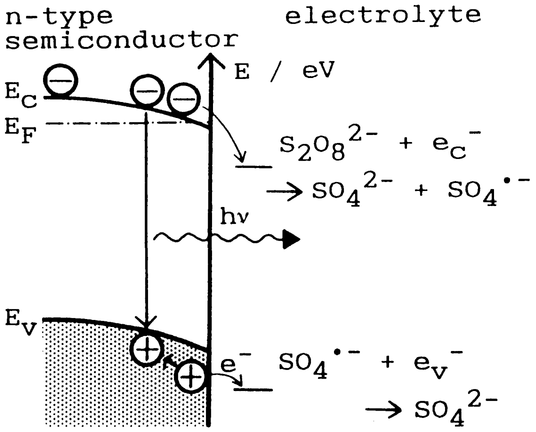

Fig. 1. Schematic energy diagram for EL on an n-type semiconductor in electrolyte containing $S_2O_8{}^{2-}$.

bias.[7,8)] In this letter, we report the enhancement of electroluminescence intensity for the porous silicon in electrolyte containing $S_2O_8^{2-}$.

Porous silicon samples were formed by anodization of n-type Si <100> of 2.4 ~ 3.0 Ω cm. The silicon wafers of 0.25 $cm^2$ area were anodized in aqueous solution of 10 wt% HF + 35 wt% $C_2H_5OH$ at 15 mA $cm^{-2}$ for 7 min under illumination using 60 W tungsten lamp from a distance of 30 cm. The porous silicon samples were rinsed and dipped in distilled water for 30 min as soon as the anodization was finished. Then it was dried in vacuum over 24 hours. EL spectra were measured at 25 °C in aqueous electrolyte solutions of 0.15 mol $dm^{-3}$ $(NH_4)_2S_2O_8$ + 0.20 mol $dm^{-3}$ $Na_2SO_4$ with and without 3.5 mol $dm^{-3}$ $C_2H_5OH$. Electrochemical cell was constructed with three electrode system of porous silicon working, Pt wire counter and Ag/AgCl reference electrodes. Potential was stepped from rest potential to various potentials of -1.6, -1.7, -1.8, -1.9 and -2.0 V vs. Ag/AgCl. EL spectra were measured by a fluorescence spectrophotometer (F-4500, Hitachi, Ltd.) with photomultiplier tube (R3788, Hamamatsu Photonics. K. K.). Immediately after starting of applying potential, the emission intensity and peak were changable. While after about 20 sec, both of the peak and the intensity were become stable. EL spectra were measured at 240 nm $min^{-1}$ from 400 nm to 800 nm and the obtained spectra were supposed as stable ones.

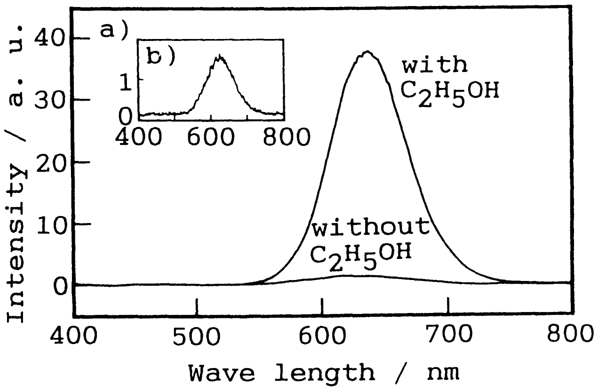

Fig. 2. EL spectra in the electrolyte with (a) and without (a, b) $C_2H_5OH$ at -1.7 V vs. Ag/AgCl.

Figure 2 shows typical EL spectra from porous silicon at -1.7 V vs. Ag/AgCl in the electrolytes with and without $C_2H_5OH$. The luminescence intensity in the electrolyte with $C_2H_5OH$ gives about 30 times as large as that without $C_2H_5OH$, and it was confirmed that the electroluminescence at porous silicon with $C_2H_5OH$ was not only stronger but also more stable than that without $C_2H_5OH$. The enhancements of stable luminescence were observed at all potentials which were observed the luminescence. The EL spectra at various potentials are given in Fig. 3. In this

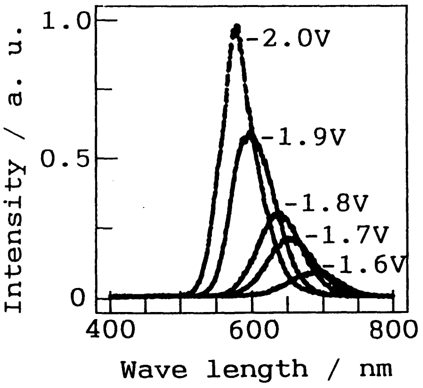

Fig. 3. EL spectra in the electrolyte with $C_2H_5OH$ at various potentials of -1.6 - -2.0 V vs. Ag/AgCl.

figure, the peaks of electroluminescence demonstrate to shift toward shorter wavelength and to become more sharp with an increase in cathodic bias. The behavior of such a peak shift for electroluminescence is just as the same as that in the electrolyte without $C_2H_5OH$ reported in the literatures.[7,8] Therefore, it is expected that adding $C_2H_5OH$ into the electrolyte induces only the enhancement of luminescence intensity. The basic idea of adding $C_2H_5OH$ into electrolyte for EL at porous silicon is to decrease hydrogen evolution which occurs with EL emission during the cathodic bias applied. We confirmed that the adsorption of evolved hydrogen gas on porous silicon surface was restrained by addition of $C_2H_5OH$ into the electrolyte. Thus, such an enhancement might come from the decrease of hydrogen gas evolution.

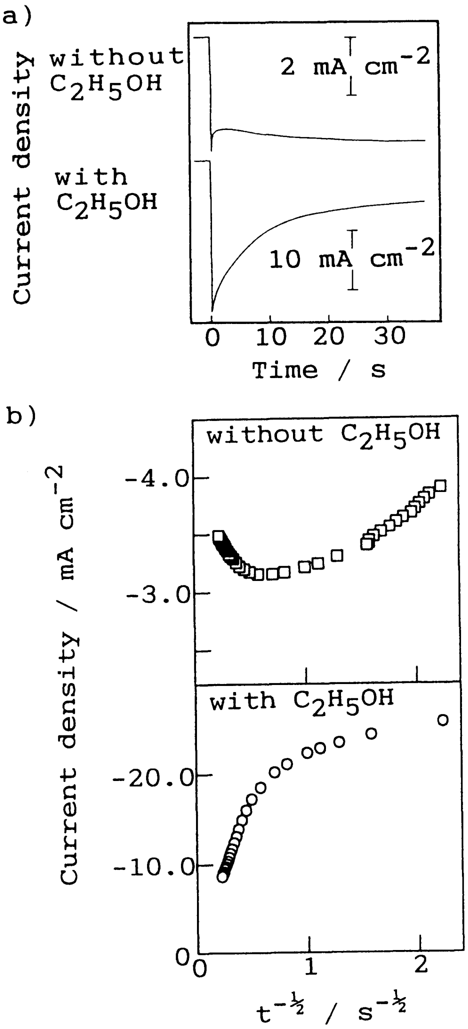

Fig. 4. Current-time profiles for EL emitting porous silicon in the electrolytes with and without $C_2H_5OH$ at -1.7 V vs. Ag/AgCl.

In order to confirm the mechanism of such enhancement of EL in detail, the time dependence of current density at -1.7 V vs. Ag/AgCl was measured during the EL emission in the electrolytes with and without $C_2H_5OH$ as shown in Fig. 4a. In the case of without $C_2H_5OH$, the diffusion controlled region of probably $S_2O_8^{2-}$ reagent is very shorter than 1 sec at the initial stage, and then the current increases a little with time is passed. On the contrary, the current decay in the electrolyte containing $C_2H_5OH$ is normal form, but its time domain is longer than that in an usual electrochemical system using aqueous solution. The Cottrell plots from the data in Fig. 4a are shown in Fig. 4b. The Cottrell plot in the electrolyte without $C_2H_5OH$ demonstrates a typical diffusion process of $S_2O_8^{2-}$ in the range of $1.5 < t^{-\frac{1}{2}} < 2.2$. While in the plot for the electrolyte with $C_2H_5OH$ two types of diffusion process are observed in short and long time ranges. The first straight line in the short time domain is attributed to the diffusion process of $S_2O_8^{2-}$ reagent from bulk electrolyte to surface of porous silicon, which is also observed in that in the electrolyte without $C_2H_5OH$. The second one in the longer time domain may be attributed to the diffusion process into the deeper parts of pores at porous silicon. The penetration of electrolyte into the minute pore might be enhanced by adding $C_2H_5OH$. It can be supported by the results that in the $Na_2SO_4$ aqueous solution the current density of hydrogen evolution at porous silicon applied the cathodic bias is enlarged by addition of $C_2H_5OH$, while at normal silicon it becomes vice versa. Also in the literatures, it was shown that porous silicon was very hydrophobic1) and the penetration of electrolyte was difficult.10) Therefore, the enhancement of EL at porous silicon in the electrolyte with $C_2H_5OH$ may be due not only to depress the hydrogen evolution but also to increase the real surface area by improving penetration of electrolyte into more minute pores. Of course, the other reasons should be considered such as enhancement of reaction (2) by stabilizing anionic free radical with $C_2H_5OH$ existence.

In conclusion, Electroluminescence in porous silicon/electrolyte containing $S_2O_8{}^{2-}$ system was enhanced drastically by only adding $C_2H_5OH$ into the electrolyte. Its luminescence intensity was about 30 times as large as that in electrolyte without $C_2H_5OH$. The adsorption of hydrogen gas on porous silicon surface during the cathodic bias applied was restrained and the two diffusion processes were observed by addition of $C_2H_5OH$.

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