Time Dependent Electroluminescence Spectra at n-type Porous Silicon/Electrolyte Solution Interface Induced by Hole Injection

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Visible electroluminescence (EL) from n-type porous silicon (PS) in an electrolyte solution containing $S_2O_8^{2-}$ was investigated by potential step methods. When the potential was stepped from 0 V to a negative potential (< -1.5 V), EL intensity increased as time proceeded. Time-resolved EL spectra measurements showed that the increase of the EL intensity was accompanied by a blue-shift of the EL spectra and that more negative the applied potential, the faster the rate of blue-shift. These results and the relationship between the emission energy and the size of the Si crystallites in PS due to quantum size effect, suggest that the emission site changed from larger sized Si crystallites to smaller sized ones in the PS layer with time.

Since Canham[1] reported visible photoluminescence (PL) from porous silicon (PS), many researches on PS have been carried out in various aspects because of possible development of Si-based optoelectronic devices.[2] The origin of the visible light emission from PS is considered to be due to a quantum size effect,[3] although other alternative models have been proposed.[4]

Most of the studies reported so far have concentrated on PL properties of PS.[5] Electroluminescence (EL) is, however, more important as far as technological applications are concerned.[2,6] Study of EL properties of semiconductor/electrolyte solution interfaces has been known to be very valuable to characterize the interface.[7] It must be also the case for PS/electrolyte solution interfaces. Visible EL under cathodically biased n-type PS in contact with $S_2O_8^{2-}$ solution have been reported by several groups.[8-10] The reduction of the $S_2O_8^{2-}$ by an electron supplied from the conduction band leads to the formation of the very reactive intermediate $SO_4^{\cdot-}$ in solution[11] which can inject a hole into the valence band of PS. Recombination between an electron accumulated at the surface in the conduction band and an injected hole in the valence band results in luminescence of band gap energy. Bsiesy *et al.*[8] reported that EL spectra of this system blue-shifted as potential was swept to more negative. We also found same phenomenon independently.[9] The origin of the blue-shift is, however, not clear.

We carried out this work to clarify the mechanism of the potential dependent EL spectra from n-type PS/electrolyte solution interface by employing potential step method and found that the EL spectra was blue-shifted with time after the potential step even when the constant negative potential was applied to PS. The more negative the applied potential, the faster the rate of blue-shift but the maximum peak energy of the spectra was almost independent of the applied potential.

PS samples were prepared by the anodization of n-type (100) silicon of 1.4 - 2.0 Ω cm in 10 % HF - ethanol solution at 5 mA/cm^2 for 300 s under illumination with 30 W halogen lamp in order to provide holes which are required for the anodic reaction to form porous structure. As-prepared porous sample was rinsed with a purified water and transferred to a spectroelectrochemical cell without exposing to air. As-prepared PS samples were used for EL measurements only once because one EL measurement altered the nature of the PS layer in certain cases.[12] EL measurements were carried out in 0.2 M Na_2SO_4 solution containing 0.15 M (M=mol dm^{-3}) $K_2S_2O_8$ in a three electrode spectroelectrochemical cell which has an optical window. An Ag/AgCl (sat. KCl) and Pt wire were employed as a reference electrode and a counter electrode, respectively. EL spectra were obtained by using a multichannel detector (Hamamatsu Photonics Co. Ltd., IMD-C3300) with an image intensifier combined with imaging spectrograph (Jobin Yvon, CP-200; f=2.9). The charge-coupled-device (CCD) elements were cooled to -20 °C. The exposure time of the CCD system was set from 0.1 to 0.2 s. The optical system is sensitive for 1.4 to 3.4 eV with resolution of 4 nm. All the electrochemical measurements were carried out in dark at room temperature.

Figure 1 shows the typical time-resolved EL spectra from PS obtained every 0.1 s after potential was stepped from 0 to -2.0 V. It is clear that the peak energy as well as the high energy

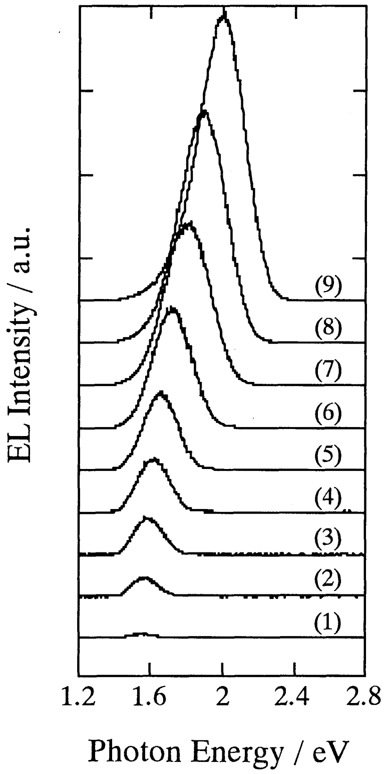

Figure 1. Time-resolved EL spectra obtained in 0.2 M Na_2SO_4 + 0.15 M $K_2S_2O_8$. EL spectra were obtained in every 0.1 s; (1) 0 - 0.1 s, (2) 0.1 - 0.2 s, (3) 0.2 - 0.3 s, (4) 0.3 - 0.4 s, (5) 0.4 - 0.5 s, (6) 0.5 - 0.6 s, (7) 0.6 - 0.7 s, (8) 0.7 - 0.8 s and (9) 0.8 - 0.9 s.

threshold of the EL spectra blue-shifted with time during a constant negative potential application but the low energy threshold was constant (ca. 1.4 eV).

Figure 2 shows the relationship between the peak energy and the time after stepping the potential from 0 V to a certain negative value. The peak energy blue-shifted from ca. 1.5 eV observed just after the cathodic polarization to higher values and finally reached a limiting value as time proceeded. It is interesting to note that the maximum peak energy was ca. 2.1 eV in all cases except for the case when potential was pulsed to -1.5 V where the negligible peak shift was observed. Clearly, the more negative the applied potential, the faster the rate of blue-shift of the peak energy. The high energy threshold showed similar trends. We emphasize here that the EL spectra from PS showed a blue-shift with time even when a constant negative potential was applied and the maximum peak energy was almost independent of the applied potential. Bsiesy *et al.* reported that the peak energy of the EL spectra changes with the applied negative potential with a slope equal to 1 eV/V.[8] They interpreted this results by considering that specific sized i.e., energy, PS are selectively excited at a given potential. Our results, however, showed that the applied potential determines only the rate of the time-dependent blue-shift of the EL spectra.

If a visible EL from PS is considered to be due to the quantum size effect of the spatial confinement of the charge carriers in the nanometer sized Si crystallites and, therefore, the EL spectrum obtained from PS reflects the size distribution of the nanometer sized Si crystallites in the PS layer and that the peak energy of EL spectrum provides the band gap energy of the Si crystallites with the most dominant nanometer size in PS layer. The fact that the peak energy and the high energy threshold blue-shifted from ca. 1.5 to ca. 2.0 eV and from ca. 1.6 to ca. 2.6 eV, respectively in all cases suggests that the PS prepared under the present condition was constituted of nanometer sized Si crystallites with band gap energies from ca. 1.4 to ca. 2.6 eV (Fig. 1). Theoretical calculation shows that nanometer sized Si crystallites of band gap from 1.4 to 2.6 eV have diameters about ca. 4.5 to ca. 2.0 nm.[13] One explanation for the blue-shift of the EL spectrum is that at the beginning of the potential pulse, the larger sized Si crystallites generate EL predominantly and the smaller sized ones starts to emit light as time proceed. The reason for this phenomenon is not clear at present.

In conclusion, we have found that the spectra of the visible EL from n-type PS in an electrolyte solution containing $S_2O_8^{2-}$ blue-shifted with time even when constant negative potential was applied to PS contrary to the results previously reported. One possible explanation for time-dependent blue-shift of the EL spectra is that the rate for the EL generation depends on the size of the Si crystallites in PS and the larger sized Si crystallites start to generate EL faster than the smaller sized one.

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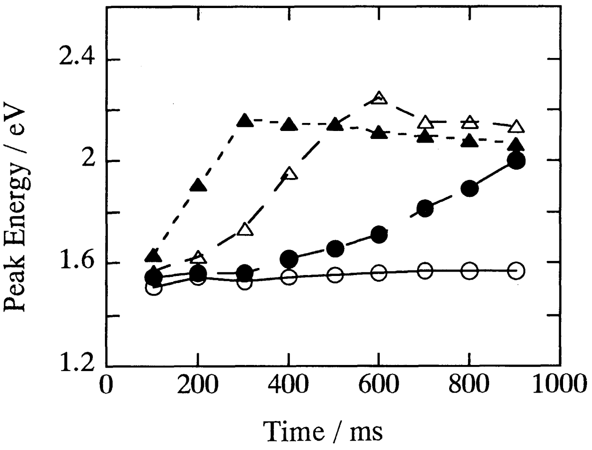

Figure 2. Time dependence of peak energy obtained from time-resolved EL spectra after stepping the potential from 0 V to -1.5 V(○), -2.0 V(●), -2.5 V(△), and -3.0 V(▲).

References and Notes

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