Fabrication of Porous Silicon-based All-solid State Multicolor EL Device with Hole Injecting Film Formed by Electropolymerization

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By using electropolymerized poly(N-vinylcarbazole) (PVCz) as a hole injecting film on porous n-silicon (PS), an all-solid state multicolor EL device on the basis of PS was able to be fabricated. The electroluminescence (EL) from the PVCz/PS device under forward bias was enhanced as compared with the device without PVCz film. An EL peak-shift of this device was observed with an increase in applied forward bias.

Since visible luminescence from porous silicon (PS) was observed at room temperature, many studies on applying this PS to new opto-electronics devices have been attempted. Until now, all-solid state EL devices have been obtained from PS, in which a carrier injecting electrode made from a metal[1] or a conducting material was formed on a PS.[2] Koshida *et al.* reported that an all-solid EL device based on PS was fabricated by using an electropolymerized polypyrrole film.[3] The device showed a higher emission efficiency than that without the conducting polymer film.

Recently, the EL peak-shift from n-type PS can be observed in an electrolyte solution containing strong oxidizing species with an increase in negative bias.[4] Previously, we also reported such spectral changes in the enhanced system of PS/ethanol-containing electrolyte interface.[5,6] This shift shows a possibility of application to multicolor EL devices using PS.[7] However, the liquid contact device is scarcely applicable to fabrication of a practical device. A solid state contact makes all-solid state EL devices preferable for practical use. In this work, we applied electropolymerized poly(N-vinylcarbazole) (PVCz) as a hole injecting film of an EL device and tried to fabricate an n-PS based multicolor EL device

The substrate used in this study was n-type silicon <100> wafer with resistivity 2.0-2.4 Ω cm. Before anodization, the wafer was cleaned, and an ohmic contact was formed by depositing thin Cr film on the back side. Porous silicon samples with double layer structures were prepared under the same conditions as those reported previously[6]; anodization current of 10 mA cm^{-2} with illumination of 3 mW m^{-2}. The PS layer thickness was about 20 μm.

The electropolymerization of N-vinylcarbazole was carried out under potential sweep mode from 0 V to 1 V vs. Ag/AgCl with various sweep rates[8]. The first scan for polymerization was so lower 2 mV s^{-1} and the second and third scans were 20 mV s^{-1}. After the third scan, the scan rate was 100 mV s^{-1} until 13th scans. The scan for polymerization was performed under illumination from the back side of this sample through thin Cr film. The reason for using such various scans is that the first scan of lower rate is for making complete formation at the inside pores. After forming the film at inside pores, faster scan was used for accelerating the growth of film thickness. The complete formation of interface between PVCz and PS was difficult and sensitive to the polymer film formation conditions, thus the formation of PVCz/PS device showed poor reproducibility. Then such a complicated process of polymer formation was adopted. The polymerization cell was assembled with PS sample (6 mmϕ) as a working-electrode, a Pt wire counter-electrode and an Ag/AgCl reference-electrode. Polymer film was prepared in acetonitrile solution containing 0.015 mol dm^{-3} N-vinylcarbazole monomer and 0.2 mol dm^{-3} lithium perchlorate as a supporting electrolyte. After this polymerization, the polymer film was undoped by applying a negative potential of -0.3 V, and the sample was rinsed in ethanol. The electropolymerized PVCz film was almost transparent.

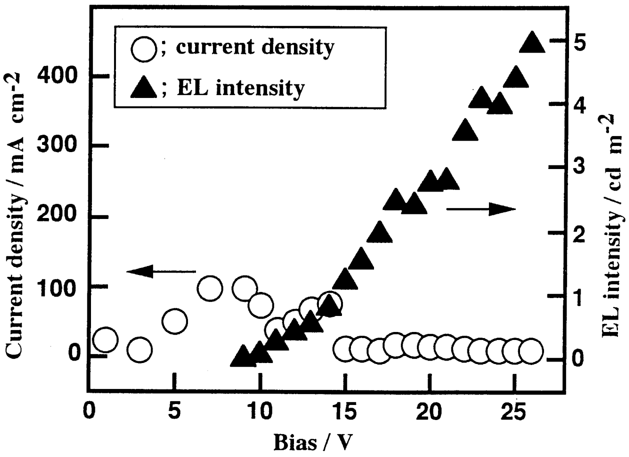

Figure 1. Dependences of EL intensity and current density of all-solid state Au/PVCz/PS/Cr device as a function of forward bias.

A gold film for ohmic contact was deposited by vacuum evaporation onto this PVCz film. The active area was 0.1 cm^2. The opto-electronic behavior was measured at room temperature in air in terms of bias-luminance, bias-current characteristics, and EL spectra. The film thicknesses of Au and PVCz were to be approximately 10 nm and 100 nm, respectively.

This fabricated PVCz/PS device showed a rectifying junction behavior, and forward bias was obtained when the PVCz film became positive with respect to grounded Si. As the positive bias was increased, the EL became visible at about 9 V under ordinary dim light, as shown in Figure 1. The current density observed at potentials up to 15 V is unclear, but it is thought to be oxidative current to make the polymer film more insulating by positive bias. When the bias was increased to higher than 15 V, the current decreased to less than 10 mA cm^{-2}, indicating effective improvement of the PVCz film. As the bias was increased, the energy efficiency also increased to the maximum value of 0.021

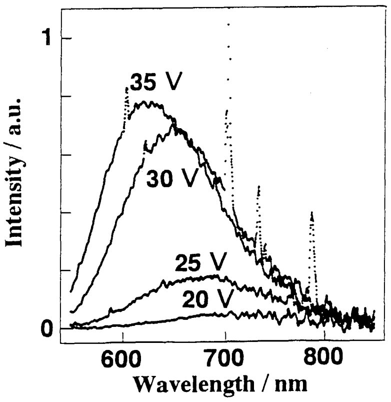

Figure 2. EL spectra of all-solid state Au/PVCz/PS/Cr device as a function of forward bias.

lm W^{-1} at 26 V. The emission is discernible under room light. No emission was observed in the reverse bias region. Lower emission was observed in the case of the PS device with only an Au contact without PVCz, which yielded an intensity of less than 0.2 cd m^{-2} at 15 V with a large leakage current of about 2000 mA cm^{-2}. Therefore, the Au/PVCz/PS/Cr device is considered to work effectively as a result of adding a hole injecting film of PVCz.

After measuring the luminance of Figure 1, the spectra of the device were measured as shown in Figure 2. After first luminance measured in Figure 1, the luminance of the device was decreased. Such a fatigue behavior was always shown to increase the measuring cycles. The spectra were measured immediately after bias application to avoid an error resulting from variation with time. The wavelength region of the emission spectra agrees with that of the PL from the PS. Furthermore, it is different from the PL spectrum of PVCz on indium-tin oxide (ITO) measured with an excitation wavelength of 250 nm. Therefore, the emission is not the EL from PVCz, but the EL from PS. With increasing bias, the EL intensity increases and the peak of the spectra shifts toward shorter wavelengths (blue-shift), as shown in Figure 2. The device with only an Au contact did not show such "blue-shift". Only at 35 V, some noises were observed, and such irregular noises might be caused by the leakage due to such a high bias. This peak shift may be caused by the improvement of the better contact between PVCz and PS, which works in the same manner as for the interface between electrolyte and PS, where the EL peak shift shows a blue-shift with an increase in bias.

In conclusion, we succeeded in the application of PVCz film as a hole injecting film to PS-based EL devices. The device demonstrated higher luminescence than the device with only an Au contact. It was also observed that, as positive bias was increased, the peak of the EL spectra shifted toward shorter wavelengths. Although further improvements are necessary concerning the voltage-tunability and the reproducibility, this spectra shift at a solid phase contact is expected to lead to multi-color EL devices.

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References and Notes

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