



POROUS SILICON LIGHT-EMITTING DIODE WITH TUNABLE COLOR

YEN-ANN CHEN,¹ BU-FANG CHEN,¹ WEN-CHIN TSAY,¹ LI-HONG LAIH,¹
MAO-NAN CHANG,¹ JEN-INN CHYI,¹ JYH-WONG HONG¹ and
CHUN-YEN CHANG²

¹Department of Electrical Engineering, National Central University, Chungli, Taiwan 32054, Republic of China

²Institute of Electronics, National Chiao Tung University, Hsinchu, Taiwan 30050, Republic of China

(Received 16 February 1996; in revised form 16 August 1996)

Abstract—We successfully combined porous silicon and amorphous silicon together to fabricate a light-emitting diode, whose emitting color was tunable with different applied voltage. When the applied voltage increased from 30 to 90 V, the emitting color of the device could change from red to blue. © 1997 Elsevier Science Ltd

1. INTRODUCTION

Crystalline Si (c-Si) has a very poor radiative recombination efficiency, since it has an indirect 1.12 eV bandgap which corresponds to an infrared emission. In 1990, Canham[1] found a strong visible photoluminescence (PL) from porous silicon (PS). In 1991, Lehmann and Gosele[2] observed an increment of the absorption edge by about 0.5 eV in PS as compared to that of bulk c-Si. Recently, many studies pointed out that PS-based devices had the potential to emit blue light[3–5]. It was believed that the increase of the band gap of PS was due to the quantum confinement in the remaining silicon quantum wire. In Ref.[6], it was also pointed out that the PS had multiple energy states, due to the quantum confinement effect, oxidized Si, defect states of SiO₂, interfacial interactions and surface states on the surface of PS, and these energy states might result in visible light emission. There were also a lot of papers[7–9] that suggested the electrons in PS could tunnel into SiO₂, SiH_x, etc. on the surface of PS, and the PS layer obtained from *p*-type c-Si wafer appeared to be a *n*-type one, because the holes in PS layer would recombine with HF⁻ during anodization, and the quantity of holes in PS layer would decrease, this would make the surface of PS layer approach 'negative'. The 'negative' PS layer having multiple energy states could be a suitable material for fabricating light-emitting diode (LED) with tunable color. That is, if electrons could be injected into those multiple energy states with higher energy on the surface of PS layer and recombine with holes from *p*-type c-Si, the PS layer would have the probability to emit light with a shorter wavelength. With these ideas, we combined porous silicon and amorphous silicon together to fabricate a LED. The fabricated

device had a energy-band diagram with a potential well, that benefited the electrons from negative electrode to be injected into those higher energy states on the surface of PS layer.

2. EXPERIMENTAL

The schematic cross-section of the proposed PS-LED is shown in Fig. 1. The employed c-Si wafer (*p* on *p*⁺, [100], 5–9 ohm-cm) was put into an E-gun evaporation system to deposit a 300 nm Al layer on its backside. Then the Si wafer was annealed at 300°C in N₂ for 3 min to obtain a better ohmic contact between the Al and *p*⁺-Si substrate. The annealed Si wafer was then cut into 2 × 2 cm² square, and the square was loaded into a vertical anodization apparatus to form the PS layer. The deposited Al on the backside of c-Si square served as the anode. A platinum sheet served as the cathode. A current density of 1.492 mA/cm² was applied for 5 min and the electrolyte was a 1:2 mixture of HF (49%_{wgt}) and methanol. The PS sample had a thickness of 1.2 μm and a PL spectrum peaked at about 675 nm as measured with an argon laser. Then the *n*-, *i*- and *p*-type amorphous silicon (*a*-Si:H) layers were deposited onto the PS layer with a photo-CVD system (SAMCO, UVD-10). After the deposition of *a*-Si:H layers, Al (4 nm) and Au (12 nm) were evaporated onto the *p*-*a*-Si:H layer with an E-gun system to form the semi-transparent electrode with an area of 0.785 cm². Then a thicker Au (100 nm) layer with an area of 0.045 cm² was evaporated onto part of device to provide a probing pad. Lastly, the sample was annealed at 300°C in N₂ for 5 min to improve the ohmic contact between the Al and *p*-*a*-Si:H layer.

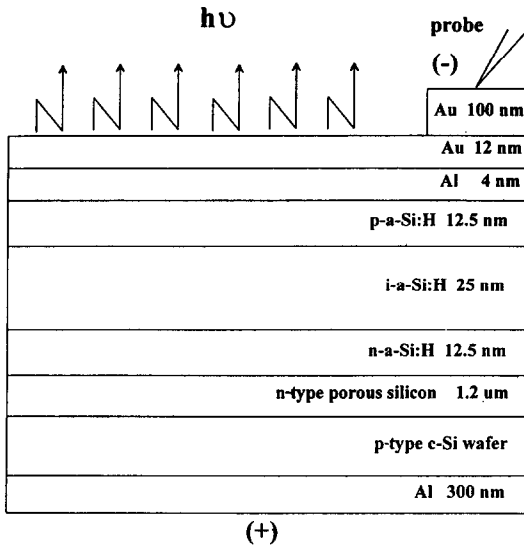


Fig. 1. The schematic cross-section of the proposed PSLED.

3. RESULTS AND DISCUSSION

Figure 2 depicts the PS-LED energy-band diagram with a potential well. When sufficient external voltage (V_{bias}) was applied, some of the electrons from the

negative Al/Au electrode would have enough energy to overcome the barrier formed by the *a*-Si:H layers and be injected into the energy states on the surface of PS layer and in the *a*-Si:H layers. For example, as shown in Fig. 2, the electron with a higher (lower) energy E_1 (E_2) could be injected into the higher (lower) energy state in PS layer (*a*-Si:H layers). The current-conduction mechanism of this PS-LED was still under investigation. Probably, it dominantly might be due to the Frenkel-Poole emission (field-tunneling injection) of electrons when the V_{bias} was low (high).

Figure 3 illustrates the various EL spectra of the fabricated device under different V_{bias} . With a lower V_{bias} about 30 V, the lower-energy electrons would recombine with holes in the *i*-, *n*-*a*-Si:H or PS layers and emitted an EL spectrum with a peak wavelength around 675 nm (1.84 eV, red color). The photon energy around 1.84 eV was close to the energy gaps of the *i*-, *n*-*a*-Si:H and PS layers. When the V_{bias} was increased to about 50 V, the electric field in the *i*-*a*-Si:H layer would be increased. Some of the electrons would be injected into the higher energy states on the surface of PS layer. So, a greenlike EL (590 nm) was observed. Further increasing the V_{bias} to around 80–90 V, the electrons would be injected into the more higher energy states on the surface of the PS

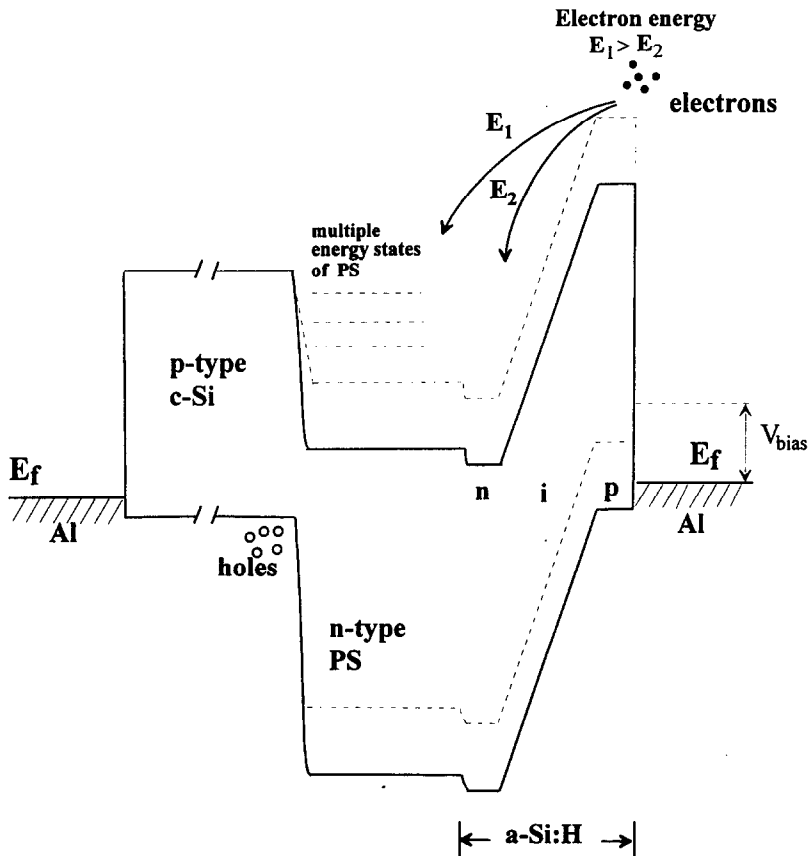


Fig. 2. The schematic energy-band diagram of the proposed PSLED. The solid line is the band diagram without applied voltage and the dash line is the one with applied voltage.

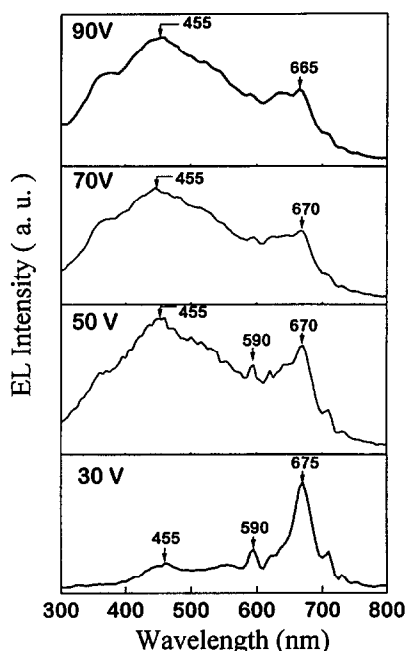


Fig. 3. The various EL spectra of the proposed PSLED under different bias voltages.

layer. This would result in a bluelike EL spectrum (455 nm) emitting from the device. So, by adjusting the bias-voltage, this device could emit light ranging from red to blue. These color lights could be seen by naked eyes in the dark. The brightness of the fabricated PS-LED was about 30–50 cd/m² as measured at a current density of 600 mA/cm². Its EL efficiency was estimated to be about 0.13%.

It was interesting that the EL spectra of the fabricated PS-LED under different bias voltages were similar to those PL spectra reported in Ref.[7]. So, in this device, the electrons with higher energy might be injected into the higher surface states in PS layer and recombine with holes from *p*-type c-Si to emit light. However, this phenomenon of spectrum shift was different from that indicated in Ref.[10], whose EL spectrum shifted with time from red to blue at a constant bias-voltage, since the EL spectrum of the fabricated PS-LED shifted only with bias-voltage and did not shift with time at a constant bias-voltage.

4. CONCLUSION

In conclusion, a novel PS-LED, whose emitting color was voltage-tunable, has been demonstrated. The EL spectrum of this device peaked at 455 (greenlike blue), 590 (green), and 675 (orange-red) nm when the applied voltage was around 80–90, 50 and 30 V, respectively. Under a higher applied voltage, the fabricated device had a blue-shifted EL peak as compared to that of the PL spectrum of the as-anodized PS sample. Although the correlation between the EL peak of the proposed device and the energy levels on the surface of PS layer was not known in detail, however, we thought the blue-shift of EL peak in this study was due to the electrons could be injected into the multiple energy states with higher energy on the surface of PS layer and radiatively recombine with holes from PS layer to emit light with a shorter wavelength under a higher applied voltage.

Acknowledgements This work was supported by National Science Council of Republic of China under contract NSC82-0417-E008-159.

REFERENCES

1. Canham, L. T., *Applied Physics Letters*, 1990, **57**, 1046.
2. Lehmann, V. and Gosele, U., *Applied Physics Letters*, 1991 **58**, 856.
3. Li, Kun-Hsi, Tsai, Chaochieh, Campbell, Joe C., Kovar, Milan and White, John M., *Material Research Society Symposium Proceedings*, 1993, **298**, 173.
4. Futagi, T., *International Conference on Solid State Devices and Materials*, Makuhari, Japan, 1993, p. 654.
5. Steiner, P., Kozlowski, F. and Lang, W., *IEEE Electron Device Letters*, 1993, **14**, 317.
6. Berhane, S., Kauzlarich, S. M., Nishimura, K., Smith, R. L., Davis, J. E., Lee, H. W. H., Olse, M. L. S. and Chase, L. L., *Material Research Society Symposium Proceedings*, 1993, **298**, 99.
7. Kontkiewicz, A. J., Kontkiewicz, A. M., Siejka, J., Sen, S., Nowak, G., Hoff, A. M., Sakthivel, P., Mukherjee, P., Witanachchi, S. and Lagowski, J., *Applied Physics Letters*, 1994, **65**, 1436.
8. Lin, J., Zhang, L. Z., Huang, Y. M., Zhang, B. R. and Qin, G. G., *Applied Physics Letters*, 1994, **64**, 3282.
9. Duan, J. Q., Yao, G. Q., Song, H. Z., Zhang, B. R., Zhang, I. Z. and Qin, G. G., *Journal of Applied Physics*, 1995, **78**, 478.
10. Steiner, P., Lang, W., Kozlowski, F. and Sandmaier, H., *Material Research Society Symposium Proceedings*, 1993, **298**, 397.