

Enhancement of electroluminescence in p–i–n structures with nano-crystalline Si/SiO₂ multilayers

D Y Chen¹, D Y Wei¹, J Xu¹, P G Han¹, X Wang¹, Z Y Ma¹, K J Chen¹,
W H Shi² and Q M Wang²

¹ National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, People's Republic of China

² State Key Laboratory on Integrated Optoelectronics, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, People's Republic of China

E-mail: junxu@nju.edu.cn

Received 25 July 2007, in final form 1 November 2007

Published 12 December 2007

Online at stacks.iop.org/SST/23/015013

Abstract

Nano-crystalline Si/SiO₂ multilayers were prepared by alternately changing the ultra-thin amorphous Si film deposition and the *in situ* plasma oxidation process followed by the post-annealing treatments. Well-defined periodic structures can be achieved with 2.5 nm thick SiO₂ sublayers. It is shown that the size of formed nano-crystalline Si is about 3 nm. Room temperature electroluminescence can be observed and the spectrum contains two luminescence bands located at 650 nm and 520 nm. In order to improve the hole injection probability, p–i–n structures containing a nanocrystalline Si/SiO₂ luminescent layer were designed and fabricated on different p-type substrates. It is found that the turn-on voltage of p–i–n structures is obviously reduced and the luminescence intensity increases by 50 times. It is demonstrated that the use of a heavy-doped p-type substrate can increase the luminescence intensity more efficiently compared with the light-doped p-type substrate due to the enhanced hole injection.

1. Introduction

Light emission from silicon-based materials, such as porous Si, nanocrystalline Si (nc-Si), silicon carbide and silicon nitride, has been studied intensively for the potential application in optoelectronic integrated circuits [1–5]. It is believed that nc-Si embedded in a SiO₂ matrix is one of the interesting candidates to develop Si-based light sources since the radiative recombination probability of electron–hole pairs in nc-Si can be obviously improved [6–8]. Room temperature photoluminescence (PL) and electroluminescence (EL) have been achieved and optical gain has also been reported previously [9]. However, considering the band offset between Si and SiO₂, the injection barrier for holes is larger than that for electrons, which results in the asymmetry injection [10] and the recombination of electron–hole pairs is hindered by the poor hole injection efficiency [11]. Therefore, it is essential to increase hole injection efficiency in order to improve the luminescence intensity.

In our previous work, amorphous Si/SiO₂ and nc-Si/SiO₂ multilayers were prepared and an intense photoluminescence was observed in regions from blue to red due to the different luminescence centers. It was demonstrated that both the quantum size effect and the surface states play important roles in controlling the luminescence behavior in the Si/SiO₂ system [12–14]. In the present work, ten periods of nc-Si/SiO₂ multilayers ((nc-Si/SiO₂)₁₀ MLs) with ultrathin oxide sublayers were designed and fabricated in a plasma-enhanced chemical vapor deposition (PECVD) system. The sublayer thickness of SiO₂ is as thin as 2.5 nm. In order to enhance hole injection, p–i–n structures with Si/SiO₂ MLs as an intrinsic layer are designed and deposited on p-type Si substrates with different doping concentrations. It is found that the luminescence intensity is significantly enhanced by using p–i–n structures. It is also demonstrated that the use of heavy-doped p-type substrate (p⁺-Si) is more efficient for improving the luminescence efficiency compared with the light-doped

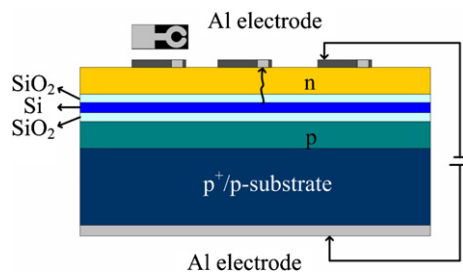


Figure 1. The schematic diagram of the LED based on p-i-n structures with Si/SiO₂ MLs as the intrinsic layer. Forward bias is applied for EL measurement. The top view of the ring-like electrode is also shown in the figure.

(This figure is in colour only in the electronic version)

(p-Si) substrate due to the enhanced hole injection into the nc-Si/SiO₂ system.

2. Experiments

Amorphous Si/SiO₂ MLs were prepared by alternating the ultrathin amorphous Si deposition and *in situ* plasma oxidation process in a conventional PECVD system with a radio frequency (r.f.) of 13.56 MHz. Silane with a flow rate of 5 sccm was used to deposit amorphous silicon and O₂ with a flow rate of 20 sccm was used to oxidize the amorphous silicon layers. The substrate temperature and r.f. power were kept at 250 °C and 50 W during the deposition and plasma oxidation process, respectively. Before the deposition, the Si wafers were etched in the diluted hydrofluoric (DHF) acid for almost 20 s to remove the native oxide layer and the metal ions.

As-deposited amorphous Si/SiO₂ MLs were dehydrogenated at 450 °C for 1 h and subsequently treated at 1000 °C for 50 s in a rapid thermal annealing system. Finally, the samples were annealed at 1100 °C for 1 h in a conventional furnace to form nc-Si/SiO₂ multilayers. All the thermal treatments were carried out in a N₂ ambient. The p-i-n structures were constructed by sandwiching the nc-Si/SiO₂ luminescent layer (as I layer) between 50 nm thick phosphorus-doped (P-doped, with a conductivity of $3 \times 10^{-3} \text{ S cm}^{-1}$) and boron-doped (B-doped, with a conductivity of $5 \times 10^{-5} \text{ S cm}^{-1}$) amorphous Si films, as is shown in figure 1. The light emitting diode (LED) was formed by evaporating Al electrodes both on the film surface (ring-like) and on the backside of Si substrates.

The microstructures of the samples were investigated by the Raman scattering technique (JY HR800) and the cross-section transmission electron microscope (X-TEM). Electroluminescence spectra were recorded by FluoroMax-2 both for p-i-n samples and for (nc-Si/SiO₂)₁₀ ML samples. It is worth pointing out that the EL signals of the samples can only be detected under the forward bias.

3. Results and discussion

Figure 2 is the X-TEM image of as-deposited amorphous Si/SiO₂ MLs. The periodic structures can be clearly identified

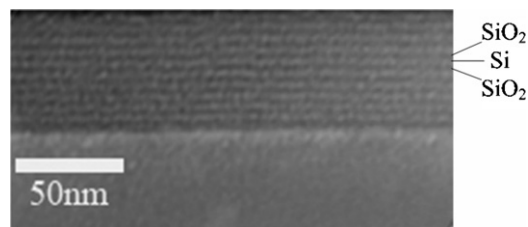


Figure 2. The X-TEM image of the as-deposited (a-Si/SiO₂)₁₀ MLs. The thicknesses of amorphous Si and SiO₂ sublayers can be estimated to be about 3 nm and 2.5 nm, respectively.

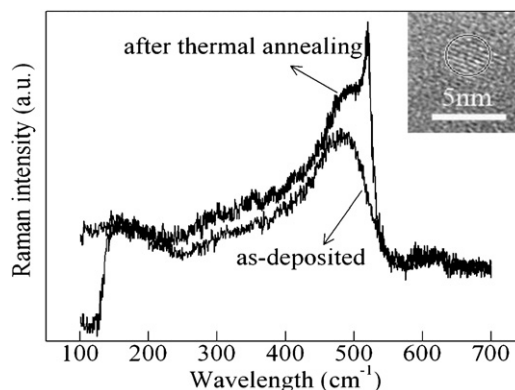


Figure 3. Raman scattering spectra of the (Si/SiO₂)₁₀ MLs before and after thermal annealing. The inset is the cross-section HRTEM image which shows the formation of nc-Si grains.

and the interfaces between amorphous Si and SiO₂ sublayers are quite flat and abrupt. The thicknesses of amorphous Si and SiO₂ sublayers can be estimated to be about 3 nm and 2.5 nm, respectively. During the thermal annealing process, the phase transition from amorphous Si to nanocrystalline Si occurs. As is given in figure 3, only the TO mode of amorphous Si (480 cm⁻¹) can be found in the Raman spectrum for the as-deposited sample. After thermal annealing, a sharp peak centered at 519 cm⁻¹ appears in the Raman spectrum, which can be assigned to the TO mode of formed nc-Si. The formation of nc-Si is directly evidenced by a high resolution transmission electron microscope (HRTEM) as given in the inset of figure 3. The nc-Si grain can be clearly seen and its size is about 3 nm which is close to the initial thickness of the amorphous Si sublayer due to the constrained crystallization principle [15].

Room temperature EL can be observed from nc-Si/SiO₂ MLs on a p-Si substrate under forward bias. The EL band is quite broad and its turn-on voltage is about 8 V. The EL intensity increases with increasing bias as is shown in figure 4. It appears that the EL spectra mainly contain two luminescence bands which are centered at 520 nm and 650 nm, respectively. The band at 520 nm can be ascribed to hot electron relaxation as proposed by the Pavese group [7, 16]. The electrons injected into Si/SiO₂ structures by Fowler–Nordheim tunneling can gain kinetic energy under a high electric field. It is reported that the holes can be generated in the oxide layer by impact ionization due to the appearance of

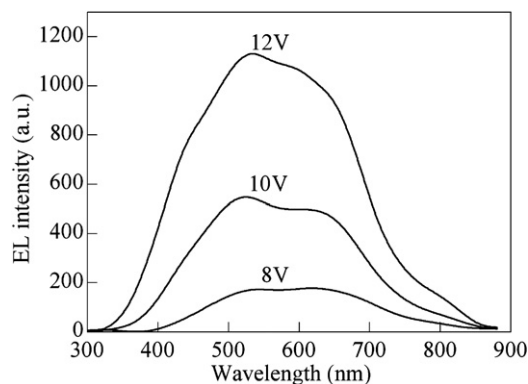


Figure 4. EL spectra of the $(\text{Si}/\text{SiO}_2)_{10}$ MLs under forward bias.

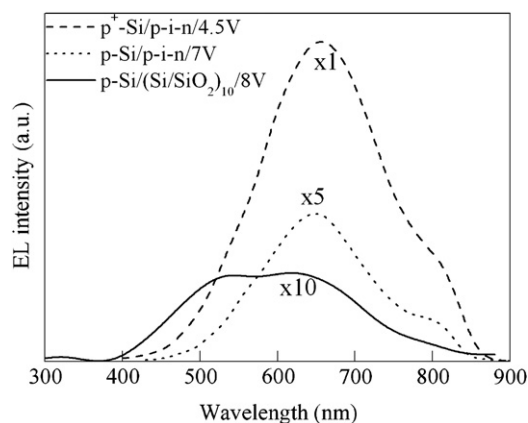


Figure 5. EL spectra of the $(\text{Si}/\text{SiO}_2)_{10}$ MLs on the p-Si substrate and the p-i-n structures on p-Si and p⁺-Si substrates. The applied biases are 8 V, 7 V and 4.5 V for various samples, respectively.

hot electrons [17]. Therefore, it is possible to get light emission via the electron-hole recombination in the Si/SiO₂ structures due to the hot electrons. It has been shown that the intensity of the band at 520 nm increases faster than that of the band at 650 nm with increasing applied voltage because the more hot electrons can be created under high voltage (therefore the high electric field) to contribute the EL signals. The band around 650 nm can be attributed to the recombination of injected electrons and holes in nc-Si/SiO₂ MLs within nc-Si and/or via the luminescence centers near Si/SiO₂ interfaces [18, 19]. A hump is also found at 450 nm in the EL spectra when the forward bias is higher than 12 V. It may be due to the oxygen vacancy defect in SiO₂ layers as suggested previously [20]. It is because the carriers can get enough energy to activate luminescence centers in the oxide layers if the applied bias is high enough. The output optical power of intrinsic Si/SiO₂ MLs was measured by using a laser power meter (460–1A) with the measurement distance of 6 cm. The maximum output power is about 10–30 nW in red (632 nm) to an infrared (1064 nm) region at the applied voltage of 10 V.

It is interesting to find that the EL spectra for p-i-n structures are quite different from intrinsic (nc-Si/SiO₂)₁₀ MLs. Figure 5 gives the EL spectra for (nc-Si/SiO₂)₁₀ MLs

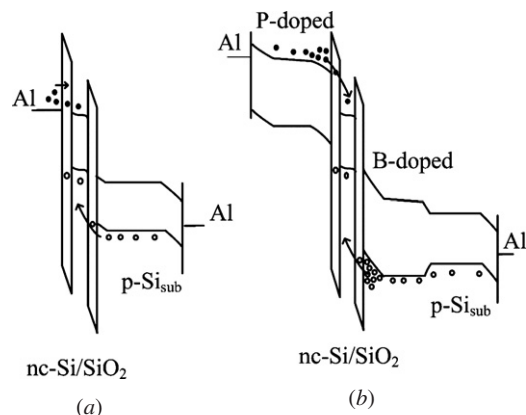


Figure 6. The band diagram of sample (a) without and (b) with p-i-n structures on p-Si, respectively.

and p-i-n structures on p-Si (with a resistivity of 2–8 Ω cm) and p⁺-Si (with a resistivity of 0.01 Ω cm) substrates under forward bias. It is found that the luminescence band peaked at 520 nm disappears and only the band peaked at 650 nm can be detected from p-i-n samples, which indicates that the dominant recombination process in p-i-n samples is the radiative recombination of injected electron-hole pairs in the nc-Si/SiO₂ system. A hump is also found at 820 nm in EL spectra for p-i-n samples. The origination of this band is still unclear at the present stage. A possible explanation is attributed to the emission from amorphous Si [21]. By using p-i-n structures, it is found that the turn-on voltage is obviously reduced compared with that of intrinsic nc-Si/SiO₂ MLs. The EL signals can be detected under forward bias from 5 V for p-Si and 3 V for p⁺-Si substrates. The EL intensity is also significantly enhanced by more than 50 times for a p-i-n structure on a p⁺-Si wafer compared with that of the intrinsic multilayers as is shown in figure 5.

The improvement of EL can be attributed to the enhanced hole injection. It has been reported that the asymmetry injection of carriers in the nc-Si/SiO₂ system is caused by two factors: one is that the effective mass of the hole is larger than that of the electron, which leads to the short diffusion length of the hole, and the other is that between nc-Si and SiO₂, the conduction bands offset and valence bands offset are different, which result in the larger injection barrier for holes (4.6 eV) than that for electrons (3.2 eV). By using p-i-n structures, the injection probability of majority carriers (holes) from p-type Si substrates is increased under the forward bias as is shown in figure 6. Meanwhile, the band gap of P- and B-doped amorphous layers are wider (1.6–1.7 eV) than that of c-Si (1.12 eV), so that the tunneling barriers for carriers, especially for holes, are decreased significantly which is also helpful for improving the carrier injection.

The current-voltage characteristics for p-i-n structures on p-Si and p⁺-Si substrates are given in figure 7, respectively. It is found that the forward current is much higher for a sample on the p⁺-Si substrate than that on a p-Si substrate due to the high hole concentration in p⁺-Si substrates ($\sim 10^{19} \text{ cm}^{-3}$),

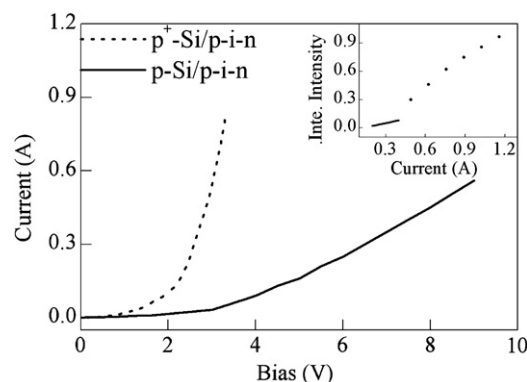


Figure 7. The current–voltage curves of the p–i–n structures on p-Si and p⁺-Si substrates. The inset gives the integrated EL intensity as a function of forward current for both samples.

which means that more holes pass through the p–i–n structures. As a consequence, the EL intensity is obviously enhanced by using the p⁺-Si substrate. Our experiment results suggest that the EL intensity is mainly controlled by the amount of the injected holes since the electron injection efficiency is high enough. The discussion is also supported by the fact that the EL intensity is proportional to the current passing through the p–i–n structures as is shown in the inset of figure 7. The slope of the curve for the sample on the p⁺-Si substrate is higher than that of the sample on the p-Si substrate.

4. Conclusion

Nc-Si/SiO₂ multilayers were fabricated by alternatively repeating the deposition of the amorphous Si layer and *in situ* O₂ plasma oxidation process followed by thermal annealing. The size of formed nc-Si is about 3 nm and the thickness of the SiO₂ sublayer is as thin as 2.5 nm. Room temperature electroluminescence was observed under forward bias from prepared nc-Si/SiO₂ multilayers. It is found that the EL intensity is enhanced by about 50 times and the turn-on voltage can be lowered to 3 V by using the p–i–n structure, which can be related to the enhancement of hole injection. The improvement in EL is more obviously for samples deposited on the p⁺-type substrate, indicating that the number of injected holes plays an important role in improving the electroluminescence intensity.

Acknowledgments

The work was supported by the National Nature Science Foundation of China (grant nos. 60425414, 90301009 and 60336010), the State Key Program for Basic Research of China (2007CB613401) and Nature Science Foundation of Jiangsu Province (BK2007135 and BK2006715).

References

- [1] Delerue C, Allan G and Lannoo M 1993 *Phys. Rev. B* **48** 11024
- [2] Zacharias M, Heitmann J, Scholz R and Kahler U 2002 *Appl. Phys. Lett.* **80** 661
- [3] Averboukh B, Huber R, Cheah K W, Shen Y R, Qin G G, Ma Z C and Zong W H 2002 *J. Appl. Phys.* **92** 3564
- [4] Xu J, Yang L, Rui Y J, Mei J X, Zhang X, Li W, Ma Y, Xu L, Huang X F and Chen K J 2005 *Solid State Commun.* **133** 565
- [5] Huang R, Chen K J, Han P G, Dong H P, Wang X, Chen D Y, Li W, Xu J, Ma Z Y and Huang X F 2007 *Appl. Phys. Lett.* **90** 093515
- [6] Franzo G, Irrera A, Moreira E C, Miritello M, Iacona F, Sanfilippo D, Di Stefano D, Fallica P G and Priolo F 2002 *Appl. Phys. A* **74** 1
- [7] Gaburro Z, Pucker G, Bellutti P and Pavesi L 2000 *Solid State Commun.* **114** 33
- [8] Heitmann J, Muller F, Zacharias M and Gosele U 2005 *Adv. Mater.* **17** 795
- [9] Pavesi L, Dal Negro L, Mazzoleni C, Franzo G and Priolo F 2000 *Nature* **408** 440
- [10] Matsuda T, Nishihara K, Kawabe M, Iwata H, Iwatsubo S and Ohzone T 2004 *Solid State Electron.* **48** 1933
- [11] Ma S Y, Wang Q Z, Wang Y Y and Liu X Q 2001 *Mater. Sci. Semin. Proc.* **4** 661
- [12] Ma Z Y, Chen K J, Huang X F, Xu J, Li W, Zhu D, Mei J X, Qiao F and Feng D 2004 *Appl. Phys. Lett.* **85** 516
- [13] Mei J X, Rui Y J, Ma Z Y, Xu J, Zhu D, Yang L, Li X, Li W, Huang X F and Chen K J 2004 *Solid State Commun.* **131** 701
- [14] Rui Y J *et al* 2005 *J. Appl. Phys.* **98** 033532
- [15] Cen Z H, Xu J, Liu Y S, Li W, Xu L, Ma Z Y, Huang X F and Chen K J 2006 *Appl. Phys. Lett.* **89** 163107–1
- [16] Pucker G, Bellutti P, Cazzanelli M, Gaburro Z and Pavesi L 2001 *Opt. Mater.* **17** 27
- [17] DiMaria D J, Cartier E and Buchanan D A 1996 *J. Appl. Phys.* **80** 304
- [18] Lin G R, Lin C J and Lin C K 2005 *J. Appl. Phys.* **97** 094306
- [19] Kanemitsu Y 1995 *Phys. Rep.* **263** 1
- [20] Liao L S, Bao X M, Zheng X Q, Li N S and Min N B 1996 *Appl. Phys. Lett.* **68** 850
- [21] Iacona F, Bongiorno L, Spinella C, Boninelli S and Priolo F 2004 *J. Appl. Phys.* **95** 3723