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ScienceDirect
Thin Solid Films 515 (2006) 775 – 777
www.elsevier.com/locate/tsf

Electroluminescence of silicon nanocrystals in p–i–n diode structures

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Available online 19 January 2006

Abstract

A new method of fabrication of nanocrystalline silicon-based light-emitting-devices is introduced. Si nanocrystals are derived from combustion or pyrolysis of silane and etched subsequently in a two-phase solution of HF. The p–i–n diodes have an active layer (20–60 nm) of Si nanocrystals sandwiched between thin isolating layers of SiO_2 or a-Si : H and a top-layer of p^+ doped silicon, the substrate being of n^+ Si. For both types of structures, electroluminescence is observed under forward bias exceeding 5 V and the spectrum consists of a broad band (due to a large size distribution of Si nanocrystals) centred around 650 nm and giving a yellowish appearance when observed by naked-eye. The integrated electroluminescence intensity growths with the square of applied bias.

PACS: 73.63.Kv; 78.60.Fi; 81.07.Bc
Keywords: Nanocrystals; Electroluminescence; Silicon; Light-emitting-diode

1. Introduction

Current research on silicon nanostructures is partly motivated by the potential fabrication of Si-based light-emitting-devices (LED) which are necessary for building up all-silicon optoelectronics. Many different LED systems containing Si nanocrystals (Si-NCs) were prepared and investigated: mainly the electrochemical etching of p–n junctions in Si wafer [1] and the Si-ion implantation of thin SiO_2 slabs in p–i–n structures [2]. The external quantum efficiency has reached about 1% [3] but the stability seems to be inversely proportional to quantum efficiency and has been preventing (up to now) application of Si-based LEDs in commercial devices. The photoluminescence (PL) of Si-NCs is, in principle, very efficient, quantum efficiency exceeding 80% was reported for individual porous Si particles [4], but for practical efficient EL structures a good injection of carriers into Si-NCs must be achieved. This is difficult due to the presence of a potential barrier which is, on the other hand, necessary for confinement of electrons and holes inside the nanocrystal and improvement of radiative recombination probability (shielding from nearby defects and increased oscillator strength). Different approaches are explored to achieve good injection into Si-NCs, for example the recent use of MOSFET transistor structure containing Si-NCs in the gate oxide [5].

In this work we introduce a new approach to prepare silicon nanocrystalline LEDs. Si-NCs, formed by combustion of silane and etching by HF [6], are placed in the p–i–n silicon structures, which show visible quasi-white EL under DC forward bias of 5 to 10 V. Here we present measurements of their electrical and optical properties.

2. Sample preparation and electrical characterization

Silicon nanocrystals are fabricated by a two step process. First, large Si nanoparticles (several tens of nm) coated by an oxide layer are grown by the combustion of silane (SiH_4) (i.e. by burning of silane in air highly diluted with argon as described previously [6] or by pyrolysis of 5% SiH_4 in H_2 heated to 1100 °C in a quartz tube). In order to activate visible PL of Si-NCs the nanoparticle size is reduced by etching with hydrofluoric acid in the two-phase cyclohexane/propanol-2 solution. The PL peak is shifting from 850 nm down to about 640 nm with decreasing size of Si-NCs (see Fig. 3B, curve c).

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0040-6090/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2005.12.190

The mechanism of PL in Si-NCs is related to the size quantization and surface state effects [7,8].

Various LED structures containing Si-NCs were prepared. Here we present two of them (see Fig. 1).

Type A: a thin layer (of about 20–60 nm) of the Si-NC (diameter of ~2–3 nm) is deposited (by dropping of suspension on the wafer) on a Si wafer (n^+) covered by a thin layer (50 nm) of n^+-doped amorphous hydrogenated silicon (a-Si:H) and a thick layer (350 nm) of undoped a-Si:H. Then the structure is covered by another layer (100 nm) of undoped a-Si:H, a 50 nm layer of p^+-doped a-Si:H, and finally a 250 nm-thick indium–tin-oxide circular contact (1 mm diameter).

Type B: a crystalline Si wafer (n^+) covered by 10 nm layer of SiO_2 (by chemical vapour deposition) is covered electrochemically by about 50 nm-thick layer of Si-NCs by immersing it to a colloidal suspension of Si-NCs and biasing it negatively. Then another layer of SiO_2 (10 nm), p^+-doped a-Si:H layer (50 nm), and a 250 nm-thick indium–tin-oxide contact are deposited on top of the structure.

The p–i–n LED structures of Type A reveal a high rectification factor of about 10^4–10^5, while the Type B has rectification factor of about 10 (see Fig. 2).

3. Electroluminescence characteristics

EL images and spectra are studied by a microscope imaging system connected to an imaging spectrograph (Jobin-Yvon Triax 320) with an intensified CCD camera (Princeton Instruments PI-MAX). The PL spectrum of Si-NCs colloidal suspension was obtained using fluorescence spectrometer Spex Fluoromax-3.

The EL signal is proportional to passing current and becomes detectable under forward bias higher than about 5 V. EL images reveal important inhomogeneity of the LED emission. Only a part of the contact area is emitting detectable EL (about 10% in best case). For bias of about 10 V the EL emission may be observed by naked-eye as white light. EL spectra are broad, covering almost the whole visible range and peaked around 660 nm (Fig. 3A, curve a). When taking into account absorbance of the top LED layers (Fig. 3A, curve c) we found the peak of internal EL spectrum is blue-shifted to about 650 nm, which is comparable to PL spectra of free Si-NCs (Fig. 3B, curve c). In Fig. 3B we compare the EL spectra

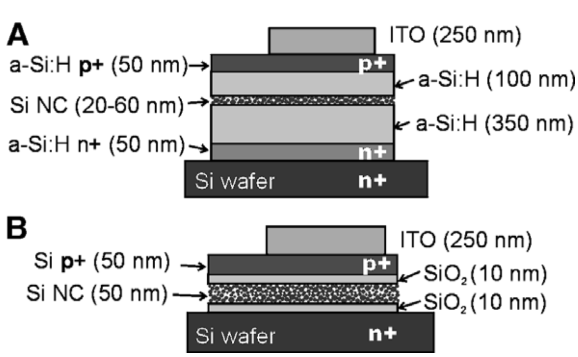

Fig. 1. Schematics of the LED structures: (A) the p–i–n structure with Si-NCs embedded between a-Si:H layers, (B) the p–i–n structure with Si-NCs sandwiched between thin SiO_2 layers.

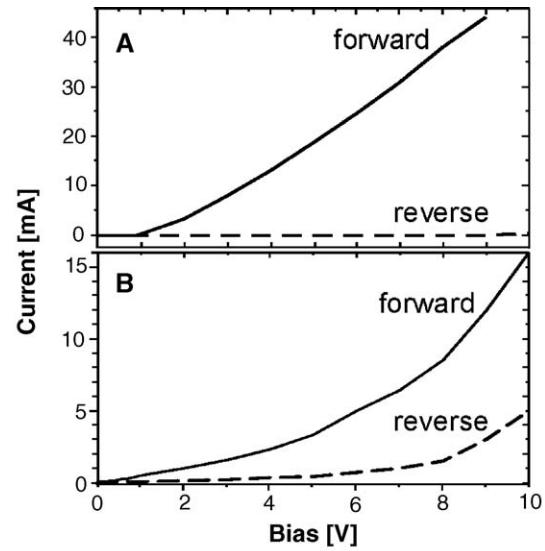

Fig. 2. Current–voltage (DC) characteristics of the two types of diodes, the solid and dashed curves indicate forward and reverse bias, respectively. (Forward polarity corresponds to negative voltage applied to the n^+ Si wafer.)

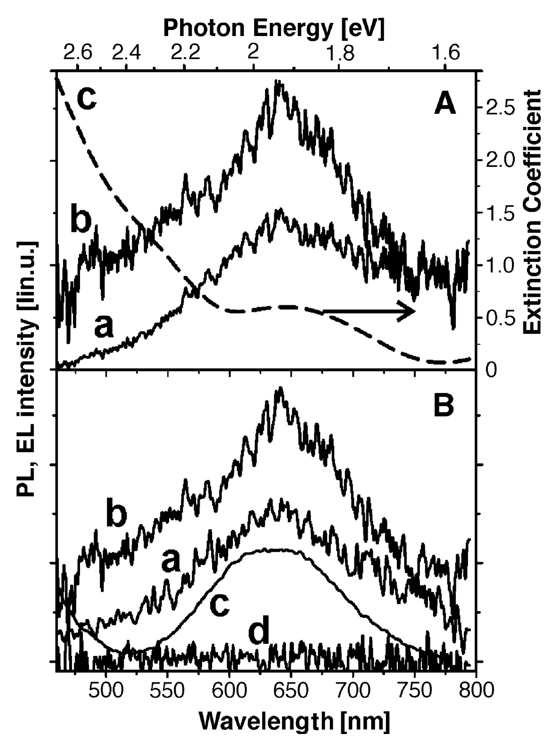

Fig. 3. Panel A: The EL spectrum of the LED of Type B under forward bias of 10 V: (a) as measured, (b) corrected for reabsorption due to the top layers, (c) extinction coefficient of the diode layers above the Si-NCs layer. Panel B: Comparison of the corrected EL spectra of LED Type A and B (curves (a) and (b), respectively) and PL spectra of the original Si-NCs in the colloidal suspension (λ_{exc}=400 nm, curve (c)). The curve (d) illustrates the EL from a LED structure containing no Si-NCs.

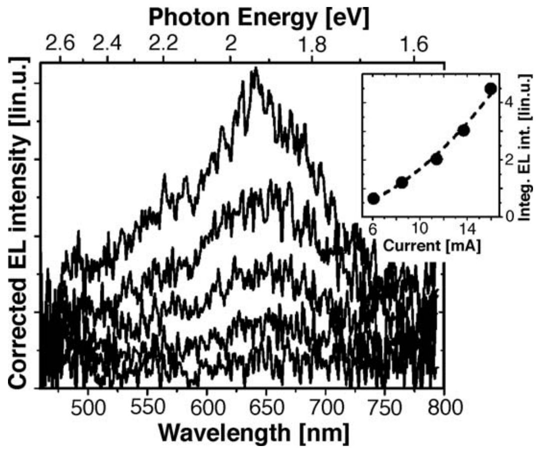

Fig. 4. Evolution of the EL spectra with increasing forward bias (7, 8, 9, 9.5, and 10 V, from bottom up). The spectra are corrected for the absorption losses in the upper diode layers. Integrated EL signal vs. current is shown in the inset. The line is a fit by function $I_{EL} = \mathrm{const} \times C^2$.

of sample of Type A and B (curves a and b) with the PL spectrum of the original Si-NCs colloidal suspension ($\lambda_{exc} = 400$ nm) and also a “blank” sample of Type B containing no Si-NCs (curve d).

Evolution of the EL spectra of sample Type B with increasing bias is plotted in Fig. 4. The plot of integrated EL intensity vs. current (see inset in Fig. 4) shows approximately quadratic dependence.

4. Discussion and conclusions

We presented a new method on how to prepare nanocrystalline silicon-based LED in the visible region. The method employs nanocrystals, derived from combustion or pyrolysis of silane and etched subsequently in a two-phase solution of HF. Good coincidence of the EL spectra in two different types of sandwich structures with the PL emission spectrum of naked Si-NCs strongly indicates that the origin of EL lies in the ensemble of the Si-NCs. The emission spectra are quite broad, obviously due to large Si-NCs size distribution. The observed quadratic dependence of EL intensity upon the forward current may indicate, according to Kanemitsu [9], a bimolecular recombination mechanism, i.e. direct injection of both electrons and holes into the Si-NCs. However, more firm conclusions can be made when completing further investigations, including application of a pulsed current excitation, the determination of external quantum efficiency and of a long-term stability.

Acknowledgements

This work was supported by the Czech Ministry of Education, Youth and Sports in the framework of the Research Plan 60840770022, Centre LC510 and by the GAAV project IAA 1010316. The research work at the Institute of Physics is supported by Institutional Research Plan AV0Z10100521. Thanks are due to Dr. J. Gurovič for assistance during preparation of the EL structures.

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