Visible electroluminescence from p-n junction porous Si diode with a polyaniline film contact

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We have fabricated a light emitting diode using a p-type conducting polyaniline layer deposited on a n-type porous silicon (PS) layer. The contact formed between a p-type conducting polyaniline layer and a n-type PS wafer has rectified behaviour demonstrated clearly by the *I-V* curves. The series resistance R_s in the p-type conducting polyaniline/n-PS diode is reduced greatly and has a lower onset voltage compared with ITO/n-PS diode. The PS has an orange photoluminescence (PL) band after coating with polyaniline. Visible electroluminescence (EL) has been obtained from this junction when a forward bias is applied. The emission band is very broad extending from 600 − 803 nm with a peak at 690 nm.

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Porous silicon (PS) has been studied intensively since the discovery by Canham[1], that even at room temperature PS can emit very bright photoluminescence (PL), in great contrast to crystalline silicon (c-Si). Owing to the wide-ranging of possible technological applications in opto-electronic devices[2−5] and biocompatible materials as well[6−7], the interest in characterizing PS has recently increased very much. Efficient electroluminescence (EL) of light-emitting diodes with a PS p-n junction has been obtained by increasing electron and hole injection into the emitting region through the incorporation of a p-n junction. Visible EL has also been observed from conducting polymer (CP)/p-PS[8]. Polyaniline is a good candidate for fabrication of a transparent conducting contact to PS. It has several advantages over other possible contact materials: it has a transmission window over part of the visible spectrum, so the thickness of material is not critical to device operation. In addition, a device can be fabricated by simple chemical based steps without requiring ion implantation to produce a p-n junction. There were some reports of successful EL from a PS/polyaniline device using a structure involving the growth of the polyaniline using a layer by layer approach[9]. We report here the fabrication of a rectifying junction between conducting polyaniline and PS. A junction between the CP and the PS using a single step process is made directly and a device with a p-n junction between polyaniline and n-PS is fabricated.

The PS samples were prepared[10] using 5.0 − 8.5 Ω n-type c-Si. Anodization was performed in an electrolyte of 1:40% HF and ethanol at a current density of 10 mA/cm^2 for 10 min under illumination by a tungsten lamp at an optical power density of 30 mW/cm^2. The total PS layer thickness was approximately 6 μm estimated from a magnified side view. The porous region is a n-PS layer. Several methods of depositing polyaniline onto the PS were tried. The best films were obtained by using a solution of polyaniline/ camphorsulphonic acid in meta creosole producing doped films in one step having a thickness of approximately 0.1 μm. Polyaniline produced by the PANi-CSA route is p-type conducting. A layer of aluminium was evaporated on the back of the substrate and annealed at 500°C to produce an ohmic contact.

To ensure that the deposition of the polyaniline does not adversely affect the electrical activity of the PS, a series of optical measurements were performed. The PL and EL spectra are obtained by transmission through a spectrometer onto a multialkali photomultiplier tube (PMT). The light is chopped and the signal from the PMT was measured with a lock-in amplifier. The excitation source is a He-Cd laser (λ=411 nm). The PL spectra before and after coating with polyaniline are shown in Fig. 1. It is clear from this figure that there is a decrease in the luminescence efficiency by 64%. This is primarily caused by absorption of the light in the polyaniline film. The fact that we can still observe luminescence on the coated PS layer demonstrates that the polyaniline does not alter the optical activity of the material. This gives support to the explanation

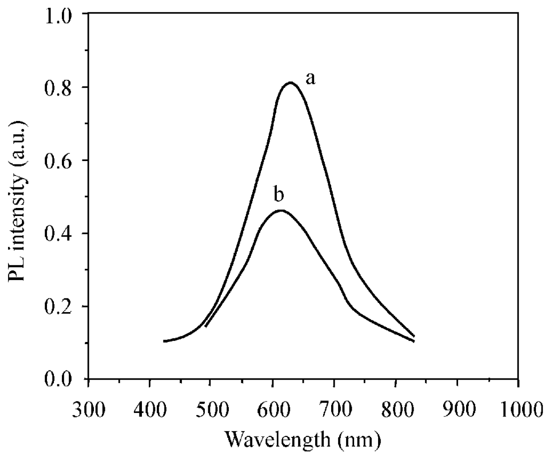

Fig. 1. The PL spectra of PS before and after coating.

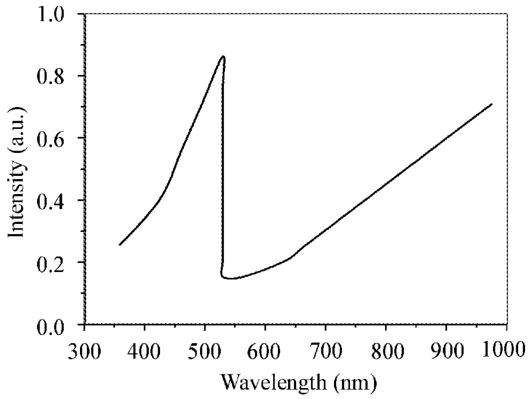

Fig. 2. Absorption spectrum of 0.12 μm polyaniline film.

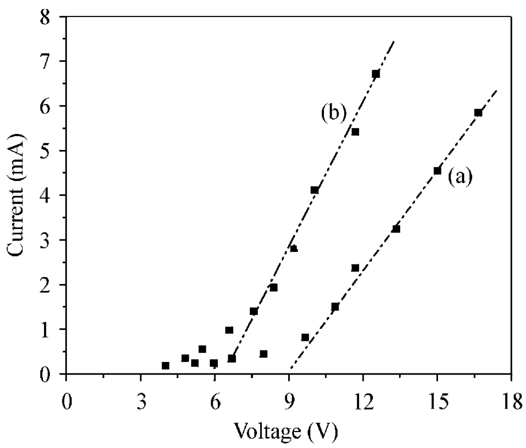

Fig. 3. Current-voltage characteristics of PS LED. Indicating presence of series resistance, the *I-V* curves of (a) an ITO/n-PS light-emitting diode and (b) a p-type conducting polyaniline/n-PS light-emitting diode.

for the origin of the red/orange luminescence band originating from the recombination in the silicon crystal nanostructures. The PL spectra before and after coating with polyaniline are shown in Fig. 1.

The absorption spectrum of a doped polyaniline film deposited on glass is shown in Fig. 2.

This film was of a similar thickness to that on the PS. The transmission window in our doped polyaniline film is close to the peak emission of the PS and it is an ideal candidate for a contacting material.

The *I-V* characteristics of the PS structure with and without polyaniline coating were studied under forward bias conditions. The *I-V* curve of a p-type conducting polyaniline/n-PS diode exhibits typical rectifying junction behavior. Similar rectifying *I-V* characteristics have also been observed from ITO/n-PS diodes. The *I-V* curves reveal that the p-type conducting polyaniline/n-PS diodes have a lower onset voltage than ITO/n-PS diodes. At room temperature, the *I-V* characteristics in Fig. 3 indicate a relatively large value of series resistance R_s for our ITO/n-PS diodes, basically due to no optimized sample preparation procedures[11] (including the ITO deposition). We note that the presence of a series resistance in ITO/n-PS diodes can limit the electrical-to-optical conversion efficiency since a portion of the applied voltage will be dropped across the resistance. We note that the series resistance R_s in the p-type conducting polyaniline/n-PS diode is reduced greatly, it is probably due to polyaniline/camphorsulphonic molecular that permeates the pore, forming better contact between p-type conducting polyaniline and inner surface of PS.

The current-voltage relationship, including the ideality factor m, can be written as

$$I = I_0 \exp\left[\frac{q}{mKT}(V - IR_s)\right], \tag{1}$$

so that the dynamic resistance of the diodes is expressed as

$$r = \frac{\mathrm{d}V}{\mathrm{d}I} = \frac{mKT}{qI} + R_s. \tag{2}$$

Clearly, when V becomes large, the first term in Eq. (2) will become negligible as compared to the second term, and the *I-V* characteristic will approach a straight line with slope R_s. Relying on Eq. (2), we corrected the characteristic to obtain the dependence of the current on the junction voltage, which indicates that the device should emit light with less than 5 V applied bias, if R_s can be eliminated ($R_s \to 0$), such as by using higher doping levels in the base silicon.

When the device was forward biased (positive applied to the polyaniline) to give a current density of $\sim$ 0.5 A/cm^2, the junction emitted visible light. The EL spectrum observed is shown in Fig. 4. The emission band has shifted further into the IR when compared with the PL spectrum in Fig. 1. The band is also broader than the PL band. The PL band has a FWHM of 165 nm and the EL band has a FWHM of 203 nm. The peak shift is from 615 nm in the PL band to 696 nm in the EL band. There is also a weaker feature in the emission band at 736 nm, the origin of this is not clear.

The EL can be seen with naked eye in day light for an operating voltage of 5 V. At 5 V, the EQE is 0.85% and the power efficiency 0.34%. This value of the power efficiency is the highest obtained to date with PS. At 6 V, the EQE is 0.98% and the power efficiency 0.30%. The power efficiency is reduced as the voltage increases even though the EQE increases. This shows the drastic influence of the voltage on the power efficiency, and highlights the necessity of using low operating voltages for getting high power efficiencies.

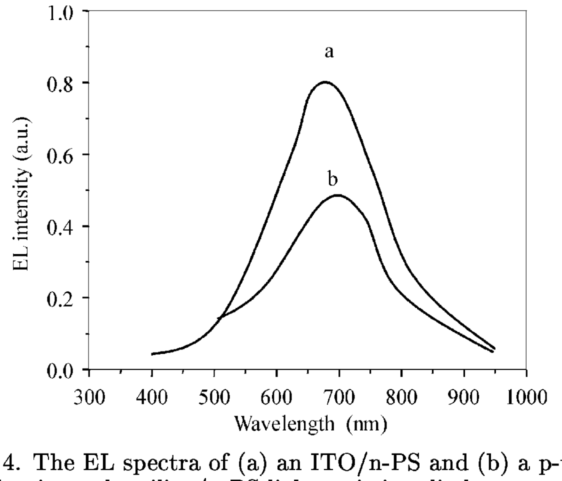

Fig. 4. The EL spectra of (a) an ITO/n-PS and (b) a p-type conducting polyaniline/n-PS light-emitting diodes.

The interface formed between a p-type conducting polyaniline layer and a n-type PS wafer was studied. The contact has rectified behaviour demonstrated clearly by the *I-V* curves. The series resistance R_s in the p-type conducting polyaniline /n PS diode is reduced greatly and has a lower onset voltage compared with ITO/n-PS diode. Visible EL has been obtained from this junction when it is placed under a forward bias.

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