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Luminescence from Porous Silicon

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ABSTRACT

Recent observations of photoluminescene (PL) and electroluminescence (EL) from porous silicon (PS) have prompted many theoretical and experimental studies. Bulk crystalline *Si* is an indirect band gap material in which recombination is dominated by non-radiative processes. Therefore, it cannot be used as light-emitting component in *Si* circuits. PS is a new material formed by anodisation of single crystal *Si* wafers in hydrofluoric (*HF*) solution. Luminescence from this material is being explored for technological applications all over the world. The mechanism of luminescence is still not well-understood. Several models have been proposed but still the facts about the strong light emission at room temperature are unknown. This paper presents a review of the fabrication process and studies on luminescent properties of PS. A hybrid model based on quantum confinement of carriers in the nanometer size *Si* crystallites having a large number of surface states is suggested to explain the observed properties.

1 INTRODUCTION

Porous silicon[1-4] (PS) has attracted worldwide attention because of the probability of integrating PS light-emitting diode (LED) into conventional microelectronics circuitry. LED will make possible to process electricity and light at the same place. According to the latest technology, light beam can carry more information and is faster than electricity. To provide these optical capabilities, development of semiconductor optoelectronics has been dominated by gallium arsenide and other III-V compounds. PS arrived at the scene[1] in 1990, and has generated much anticipation because of its property of light emission.

Silicon (*Si*) does not show luminescence due to its indirect energy band gap. But recent observations of photoluminescence (PL) and electroluminescence (EL) at room temperature has generated a curiosity among the scientists to understand the physics behind these observations.

2. FABRICATION PROCESS

The porosity in *Si* is obtained by partial anodic dissolution of *Si* wafer of one ohm-cm resistivity and <100> orientation in hydrofluoric acid (HF) and ethanol (1:1) solution[4]. Back side of the wafer is coated with *Al* by vacuum evaporation technique and is protected by acid resistant wax during anodisation. The anodisation current is kept between 10 and 15 mA/cm^2. This process produces a nanometer size ligament network in the *Si* wafer. The thickness of the porous layers, thus formed, is 25 μm. The *p-n* junction has been made in PS by a new technique proposed by Jain, *et al*[4,5]. The p^+n and n^+p junctions were made by diffusion of counter dopants in PS at high temperatures. The diffusion of *P* in *p*-type PS from $POCl_3$ source and

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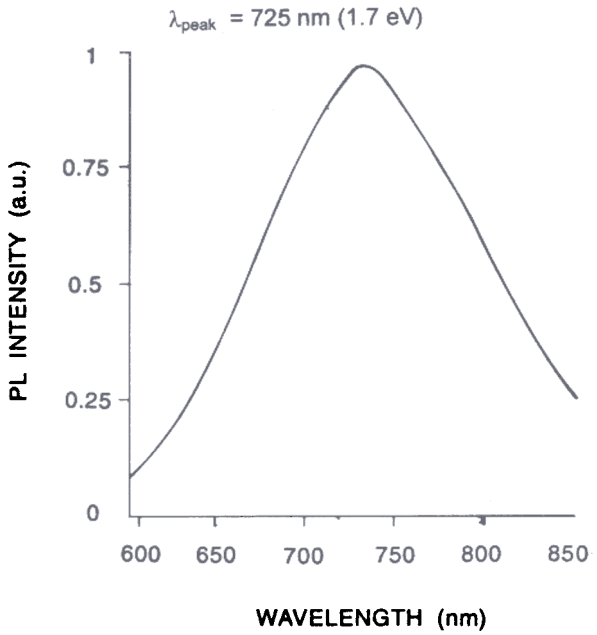

Figure 1. Photoluminescence spectrum of *p*-type porous silicon excited by an Ar^+ laser (488 nm).

B in *n*-type PS from a *BN* solid source is carried out at 850 °C and 975 °C, respectively. This forms n^+p and p^+n structures. The high-low junctions p^+p and n^+n have also been made. Secondary ion mass spectroscopy (SIMS) analysis shows that carrier concentration in the doped region is about 10^{20} atoms/cc. In these studies, it is difficult to find out the depth of the junction, because of the porous property of the material.

3. PHOTOLUMINESCENCE

Visible PL is the most important and commonly observed property of PS. Generally, a bright red or orange glow can be seen by placing the sample in ultravoilet (UV) light. The PL spectrum (Fig. 1) is taken by exciting the PS samples with 488 nm Ar^+ laser. It has been seen that the PL intensity of PS decreases sharply on annealing at >300 °C. Fourier transform infrared (FTIR) measurements show that *H* gets desorbed from the *SiH* species at this temperature. Jain, *et al*[4]. reported the first observation of PL from porous silicon after counter doping by diffusion at high temperature (850- 1000 °C). In these investigations, PL was found only in n^+p and p^+n junctions and not in high-low n^+n or p^+p junctions in PS.

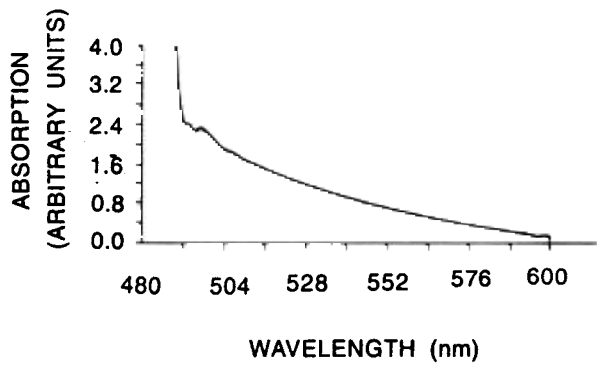

Figure 2. Absorption spectrum of porous silicon

4. BAND GAP MEASUREMENT

Windows of PS of 400-800 μm diameter have been made by waxolithography[5] in 280 μm thick *Si* substrate. This is achieved by controlled etching and porosity is generated in these windows to 25 μm thick porous dots and no substrate is left. After removing the wax, these dots glowed from the front as well as from the back under UV light and also gave a bright red glow through transmission, when illuminated by visible collimated light. These windows have been used to measure the band gap of PS. The absorption spectrum (Fig. 2) shows a sharp edge at 2.56 eV where the absorption coefficient is enhanced by several orders.

5. ELECTROLUMINESCENCE IN POROUS SILICON LIGHT-EMITTING DIODES

Observation of PL in *Si* is an exciting phenomenon, but the development of optoelectronic devices require that the material should respond to electrical energy. Therefore, all efforts are aimed at making material more sensitive to electrical energy. Another major problem is to choose the proper material for making metallic contacts with this material. Our studies on ohmic contact with *p*-type or *n*-type PS show that the three layer structure of *Ti/Pd/Ag* (*Ti* = 200 Å, *Pd* = 200 Å, and *Ag* = 1 μm) provide a good ohmic contact. In case of *p*-type *Si*, *Al* is also used to make ohmic contact.

Richter[2], *et al.* and Koshida and Koyama[3] studied EL by making metal-Schottky contact with PS layer. Richter, *et al.* found EL peak at 680 nm

when a current of 5 mA was passed through the sample at 200 V. Koshida & Koyama found the rectifying behaviour in this junction and EL peak at 680 nm. Namavar[6], *et al.* observed EL in indium tin oxide (ITO) PS-*Si* Schottky like structures, but these devices give feeble and unstable EL. Recently, Chen, *et al*[7]. observed the visible light emission from PS homojunction. They made a $n^+ p^+$ junction by ion implantation in PS wafer. The porosity was generated after the junction was formed. The EL was seen through a 100 Å semi-transparent gold layer.

Later, Steiner, *et al*[8]. also made a diode with PS following the same technique of ion implantation in wafer and then generated the porosity in the junction. On application of low voltage, the light emission was seen through the thin metal pads. At higher voltages (25 V), red-orange glow was seen with naked eye but within minutes, the series resistance increased that caused a decline in light intensity. Lee and Peng[9] formed blue LEDs in PS. The emission has again been observed through the semi-transparent gold electrode.

A stable, very bright red coloured EL in n^+ -*p* and p^+ -*n* junctions, made by diffusion in PS, on application of 5 V and 300-400 mA current was reported by Jain, *et al*[4]. for the first time. The important observation is the brightness and stability of the EL. The voltage was applied across the junction in forward direction. The exact power requirement can be predicted only after optimising many factors like area of PS, contact resistance, contact materials, etc. Presently, efforts are in the direction to reduce the total power consumption. Moreover, the sample when kept at liquid nitrogen temperature gives continuous bright EL for an indefinite period. It was also observed that high-low junctions, i.e. p^+p and n^+n in PS do not give EL.

6. MODELS

Several models[10-12] have been proposed by various scientists, but still the facts about the strong light emission at room temperature are unknown. One group of scientists believes that PL has a chemical origin, resulting from the formation of molecules on the large surface area of PS. Many compounds have been suggested. One of the suggested candidates is the hydrogenated amorphous phase[13,14] of *Si*. It is evident that *SiH* complexes can give visible PL at room temperature and the optical band gap of the binary *Si:H* materials increases almost linearly with the increasing hydrogen content. The same concept can be extended to PS. Another group[15] favours siloxene ($Si_6O_3H_6$) and its derivatives. Six- fold *Si* rings in siloxene structures play the key role in their luminescent property.

Some experimental observations are against the presence of *Si:H* or siloxene compounds on the surface of the *Si* which are responsible for the PL at room temperature. X-ray analysis shows that lattice structure of PS is same as that of *Si*, except some expansion. These models cannot explain the occurrence of strong PL, when samples are prepared[16,17] such that they have no *H* or *O*. This seems that *O* and *H* are not the essential constituents in PS for PL in visible range. High temperature treatment between 800-1000 °C during oxidation and formation of *p-n* junction bring back PL in these samples. The temperature treatment also confirms that hydrides of *Si* or siloxene compounds cannot stand such high temperature.

One of the most widely suggested concept is based on quantum confinement. PS structures consist of *Si* wires, and as the porosity is increased, the thickness of the wires decreases to nanometer sizes. These nanostructures are expected to have a direct band gap, sufficiently large, to give visible light. The transmission electron microscopy (TEM) shows that wafers of PS having 80 per cent porosity have average wire width between 30 to 40 Å. Calculations of electronic structure of hydrogen-terminated *Si* based on pseudopotentials show that 30-100 Å diameter wires result in direct band gap at zone centre due to upshifting of conduction band minima by a large amount of energy[18]. Support to this model comes from the observed blue shift of PL peak for longer etching conditions before or after oxidation. Attempts have been made to deliberately

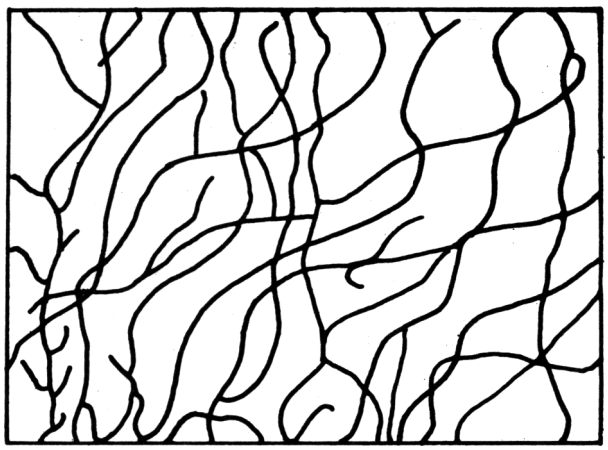

Figure 3. Interlinked quantum wires in porous silicon

change particle size to verify the quantum size models. This is done by further etching in dilute *HF* or dry oxidation at high temperature. These samples show blue shift which is consistent with quantum model.

Though the quantum size model explains some of the properties of PS, it fails to explain many other observations. No direct relationship between particle size present in PS and visible PL has yet been established. Samples with less than 20 per cent porosity having wall thickness 200 nm also show visible PL. The quantum size model also cannot satisfactorily explain the reduction in PL on heating up to 400 °C. Change in PL spectra on selective chemical treatment also cannot be explained by this model. This quantum confinement model is also unable to explain the observations of PL in n^+p or p^+n junction and not in p^+p or n^+n (high low) junction.

Here, a hybrid model is suggested to explain phenomenologically, the properties of PS. It is assumed that PS has a spongy-type structure composed of an interconnected network of quantum size *Si* wires (Fig. 3). According to Wilshaw and Boswell[19], the structure is coral-type and TEM of such PS shows that some of the ligaments, which terminate at the surface, actually protrude from it in the form of fibrils. The length of these ligaments is 100-200 Å and the diameter is down to 30 Å. The surface of these wires is passivated with *H* which reduces surface recombination. By changing the

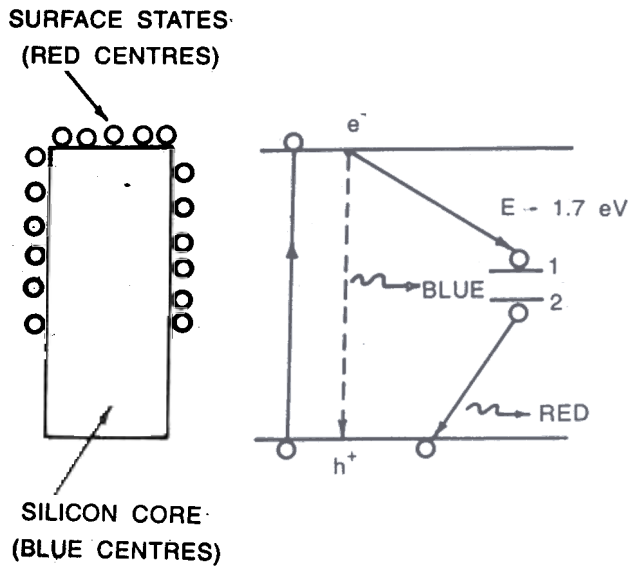

Figure 4. Energy states in *Si* quantum wire

diameter, one can change colour of emission. The defect states, which originate PL in PS, could be the surface states on enormous area of PS. This has been suggested by many workers. On oxidation at high temperature, PL shifts from red to blue. To understand the basic phenomena for this change from red PL to blue PL, though many concepts were given but it is concluded that there are two types of centres responsible for PL in PS. Red centres are due to states which give PL near 700 nm while blue centres are due to core of the *Si* wire. The origin of red centres is different from that of blue centres. Various concepts have been proposed for these different types of centres.

An energy model[20,21] (Fig. 4) explains these concepts. In this energy model, one represents a nanocrystalline *Si* core state and the other levels (1 & 2) in between the band gap are due to surface states on nanocrystalline *Si* core. The enhancement of band gap from 1.1 eV to 2.6 eV is due to the quantum size effect. Recently, Zhao, *et al*[22] demonstrated the intense violet and blue emission at 415 nm, 437 nm and 465 nm at room temperature from nanocrystalline *Si* films.

After anodisation, these films show PL in violet to red colour emissions. Demonstration of blue luminescence in these nanocrystalline films of

grain size 30 Å without anodisation showing blue and violet emission is the evidence of zero-dimensional quantum confinement effect.

According to Laiho, *et al*[21]. after excitation, part of the electrons and hole are quickly recombined at State 1 and part of the carriers are trapped to State 2 (Fig. 4). Mimura, *et al*[20]. also explained that during excitation, carriers are photogenerated in the nanocrystalline *Si* core and then transferred to surface states before recombining radiatively.

This model has two probabilities for recombination of carriers: (a) through surface states (b) by direct radiative recombination. But when the energy-band gap due to surface states, is smaller in comparison to *Si* core, the efficiency of radiative recombination through surface states is high and peak is observed in visible region. When the band gap of the *Si* core is smaller than due to surface states or in absence of surface states, the recombination in *Si* core is more probable due to the quantum confinement and efficiency in blue region is more than red region. Laiho, *et al.*[21] found that in visible region, there were two emission bands in their sample with maximum at 630 nm and 680 nm. Dneprovskii, *et al*[23]. also observed two optical transitions at 735 nm and 620 nm during their measurement on time-resolved nonlinear transmission spectra by picosecond spectroscopy. Jain, *et al*[4]. observed two peaks in their PL measurement. This proves that there are many energy levels existing in this enhanced energy gap.

The enhancement in band gap is due to quantum confinement which is supported by the observations during oxidation of PS and measurement on carrier lifetime in PS as discussed here.

Kovalev, *et al.*[24] found that for samples oxidised below 700 °C, red luminescence is quenched by two orders of magnitude, while blue component is intact. This may be due to stripping of *H* from the surface and increase in nonradiative recombination. Oxidation between 700–800 °C recovered the red component. This replaces the *H* by *OH* or *O* atoms, but it cannot migrate into *Si* network. Calculations show that it has *SiO* or *SiOH* and band gap is 1.7 eV. On further oxidation between 800–1100 °C, *O* migrates into *Si* network forming SiO_x, which has a higher band gap of 8 eV. This PS gives only blue luminescence and the result has been confirmed by many groups. It also suggests that carriers generated in *Si* core cannot be transferred to surface states as the band gap difference between PS*i* core and SiO_2 layer is very large. All the carriers recombine through quantum confinement, like in quantum dots, giving only blue response.

Several experiments have given two lifetimes in these samples, one is very fast and the other is slow. Lifetime of red component is between 1-10 μs. Xie, *et al.*[25] reported 10 μs. for samples prepared having peak corresponding to 1.7 eV and 1 μs for samples having PL peak at 2.1 eV. This slow component of lifetime correspond to the levels in the energy gap due to surface states in porous layer. Another component is very fast, at least three orders faster than red component with no dispersion. At first sight, the blue PL appears to be a different type of phenomenon. Kovalev, *et al.*[24] measured the lifetime of blue light ~ 6.5 ns which is also known as fast band and lies between 2.2 eV to 2.6 eV.

In the case of EL, Koshida, *et al.*[2] have used the semi-transparent top contact of *Au* which forms a Schottky contact with PS. When the applied voltage is sufficiently high, electrons from top contact and holes from the *Si* substrate are injected in porous layer by tunneling effect. These carriers recombine and emit light.

In these experiments on EL, the Schottky junction has been replaced by making a p^+n or n^+p junction in porous layer by counter diffusion of impurities at high temperatures. The carriers are transported more efficiently by diffusion instead of tunnelling and their radiative recombination in thinned *Si* wires is possible at low voltage and current. After diffusion of *P* in *p*-type PS, it forms junction in *Si* wires as shown in Fig. 5. Earlier[4], it was considered that the diffusion of impurity

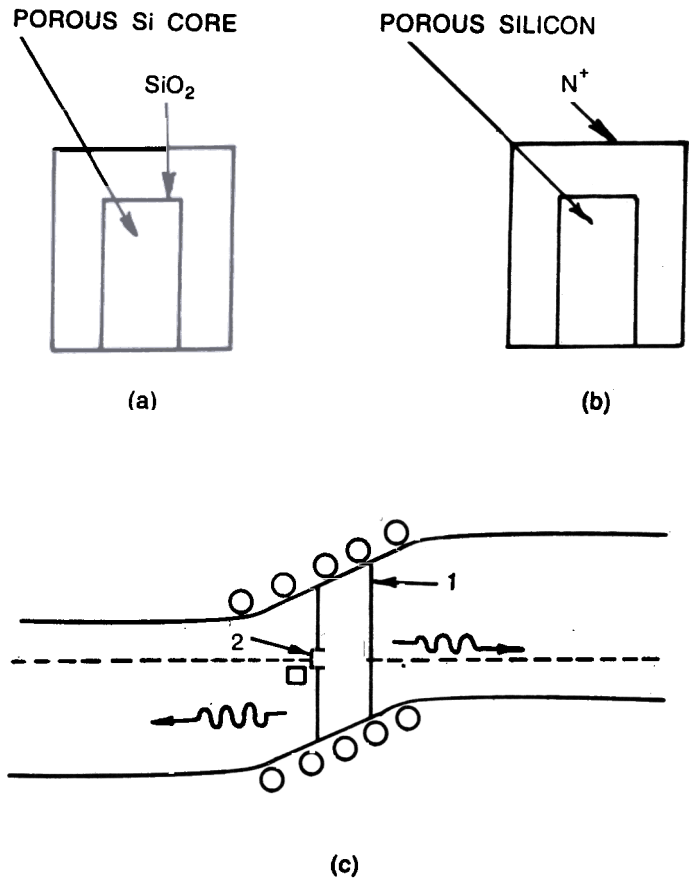

Figure 5. Model for porous silicon: (a) after oxidation, (b) after diffusion, and (c) electroluminescence from diffused *p-n* junction in porous silicon.

occured from all sides of *Si* wire and the *Si* wire would be heavily doped. However, it is possible that diffusion phenomenon is different in *Si* wires than in plain *Si* wafer due to limited number of free states available just like oxidation in these wires[24]. It was observed that during oxidation at 1000 °C, SiO_2 is formed at the surface but *Si* core remains as shown in Fig.5, although oxidation time and temperature is sufficient to fully oxidise the 40 A° *Si* wire. Hence, the junction is formed around the *Si* wire. In these structures the process of recombination changes completely and on illumination and also during application of small voltages, PL and EL occurs in the depletion region of the junction. It also explains that by making n^+n and p^+p high-low junctions, why there was no PL and also no EL. Here, the barrier is very small and no recombination of carriers occurs. This explains the phenomenon clearly how a junction is helping in EL. It also confirms that when there is no junction but semi-transparent electrode, Schottky barrier is formed between *Si* wires and top electrode, and because of large collection area and high voltage across the top and bottom electrodes, only feeble EL is observed. Due to efficient phenomenon, a bright EL was found in *p-n* junction.

7. CONCLUSION

Observation of luminescence from PS in the visible region at room temperature has opened a new era in optoelectronics for integration of a light-emitting device of *Si* with the existing *Si* integrated circuit (IC) technology. Various structures are being tried to improve the efficiency of EL. Several models have been proposed but none can explain all the properties of PS because it is a complicated system having large number of surface & bulk defects together with a network of interlinked quantum wires of *Si* which are responsible for its characteristic luminescent properties. Here efforts have been made to propose a hybrid model to understand the bright PL and EL phenomenon in PS.

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