OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 10, No. 9-10, September-October 2016, p. 689 - 692

# Enhanced photoluminescence from porous silicon by rare earth doping and DBR structures

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We report a new way to enhance the photoluminescence of porous silicon(PS) in red light(625 nm) under room temperature by doping the rare earth(Yb) in porous silicon with distributed Bragg reflection (DBR) structures. It is observed that a suitable concentration of $Yb^{3+}$ ions could enhance the photoluminescence of porous silicon effectively. Compared with the single-layer porous silicon film, the enhancement of Yb-doped PS photoluminescence from porous silicon DBR structures is higher. RE doping and DBR structures could double strengthen PS photoluminescence.

(Received June 3, 2015; accepted September 29, 2016)

*Keywords:* DBR structures, Photoluminescence, Porous silicon, Rare earth

## 1. Introduction

Due to the strong room-temperature photoluminescence (PL) from porous silicon (PS) [1] observed in 1990, worldwide interest have been attracted to silicon-based photonics for integrated optoelectronics. However, the application of porous silicon as one of the main candidates for silicon-based light-emitting devices is hindered because of poor stability of PL and low luminous efficiency.

Great efforts have been made to overcome these drawbacks, which mainly contain three ways. The first one is treatment based on prepared PS, for example, Wang et al. deposited Au nanoparticles on porous silicon and enhanced luminescence of PS due to localized-surface-plasmon (LSP) resonance [2]; Jarimavičiūtė-Žvalionienė et al. treated the PS film with selenious acid [3]; Wang et al. etched the PS with hydrogen-plasma [4]; Harraz et al. [5] and Filippov et al. [6] doped conducting polymers and rare earth on PS, respectively. The second one is the development of the preparation method of PS, for example, enhanced photoluminescence was obtained by preparing PS on crystalline silicon wafer with co-doped of $Si^+$ and $C^+$ ions in Fu et al. report [7]; In the study of Lin, n-type porous silicon (n-PS) films are prepared with the assistance of Hall-effect during the electrochemical anodization [8] and PL emission of n-Si can be drastically enhanced. The third one is PL enhancement of porous silicon by making PS with special structures, for example, Lorenzo Pavesi et al. enhanced the PS photoluminescence by photonic crystals structures [9].

Enhancing the photoluminescence of porous silicon in visible range by doping rare earth is widespread due to the low cost, few time and easy to achieve. However, the substrates they used are single layer porous silicon [6, 11].

The Bragg structures of porous silicon prevent the propagation of electromagnetic wave within the band-gap area and this characteristic can improve the PL of porous silicon. However, to our knowledge, there are not any research about improving PL of RE doped porous silicon using DBR structures.

In this work, we doped rare earth into porous silicon with DBR structures and studied the effect of the structures on the enhancement of photoluminescence. A rare earth element we need to choose which is no fluorescence in the visible range. The Ytterbium(Yb) is a good candidate due to its fluorescence in 920-1100 nm when the $^2F_{5/2}(Yb^{3+})$ relax radiatively to the $^2F_{7/2}$ [10]. We deposited rare earth on porous silicon by constant-potential ECD [11]. Compared with their fluorescence, the Yb-doped PS fluorescence is stronger than PS, and Yb-doped porous silicon Bragg reflectors fluorescence is significantly higher than single-layer porous silicon films with Yb.

## 2. Experiments

### 2.1. The preparation of porous silicon Bragg reflectors

The porous silicon Bragg reflectors were prepared by changing the electrochemical etching parameters to form the periodically changing porosity (or refractive index). A band-gap area with high reflectivity is the biggest feature of porous silicon Bragg reflectors. Each layer of film satisfies the following relationship [12]:

$$m\lambda_{Bragg} = 2(n_L d_L + n_H d_H) \tag{1}$$

where m is a Integer, $n_L(n_H)$and $d_L(d_H)$ are the low(high) refractive index and thickness of the porous silicon layers respectively. $\lambda_{Bragg}$ is the center of the band-gap.

A PS Bragg reflector with a band-gap center at 670 nm was designed. The reason is that the fluorescence peak of single layer PS we fabricated at 620 nm and the band-gap will blueshift after oxidation and redshift after doping. The band-gap area should include the emission band of the single layer PS. The porous silicon sample was fabricated using p-type Si(100) with resistivity of 0.03-0.06 $\Omega\cdot cm^{-1}$. The solution that mixed by hydrofluoric acid (HF 40%) and ethanol (95%) (1:1 by volume) is used as the etchant to form porous silicon. The DBR structures of 10 periods was fabricated with an alternating current density of $I_H$=100 $mA\cdot cm^{-2}$ and $I_L$=60 $mA\cdot cm^{-2}$, and the etching times of each layer was 1 s and 1.2 s. The thickness of the finished PS films are about 2 μm. Then the single layer porous silicon of the same thickness for comparison is prepared by the current density of 100 $mA\cdot cm^{-2}$. Finally, all samples were oxidized by immersing in hydrogen peroxide (30%) at 60 ℃ for 3 hours and dried in air.

### 2.2. Rare earth deposited on porous silicon samples

The prepared PS samples were immersed in a certain concentration mixed solution of $Yb(NO_3)_3$ and acetonitrile. A negatively biased current relative to a platinum electrode in a similar arrangement to that used for the previous etching step. The applied voltage was fixed at 4 V for a certain time. Then the samples were rinsed with deionized water and dried in air.

### 2.3. Detection of sample

The spectrum of reflection and fluorescence was detected by a Spectrophotometer(Hitachi U-4100,Japan) and a fluorescence spectrophotometer(Hitachi F-4600,Japan), respectively. A fixed excitation wavelength of 380 nm was used and emission spectrum was measured in 500-750 nm. Morphology of porous silicon Bragg reflectors was detected by a ZEISS SUPRA55 VP scanning electronic microscope (SEM).

## 3. Results and discussion

Fig. 1 shows that the pore size of porous silicon is approximately 40 nm. The Light-colored substance on the surface is doped rare earth and the different levels aggregation occurred. Particle size ranging from a few nanometers to several hundred nanometers. Using Energy Dispersive Spectroscopy(EDS) analysis, we determined the concentration of $Yb^{3+}$ ions as 1.8%.

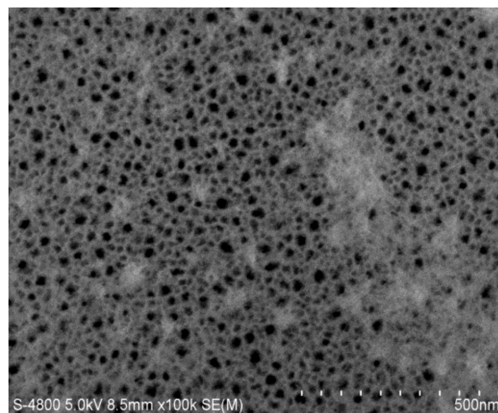


*Fig. 1. Top-view SEM image of Yb-doped porous silicon Bragg reflector*

Fig. 2 shows the cross-sectional view SEM image of $Yb^{3+}$ ions infiltrated into porous silicon Bragg reflector. The dark colored PS layers were formed by etching with a current density of 100 $mA\cdot cm^{-2}$ and the light colored layers were etched by 60 $mA\cdot cm^{-2}$. The thickness of each layer is about 100 nm.

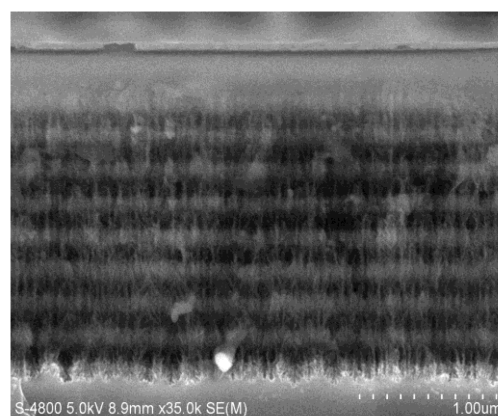


*Fig. 2. Cross-sectional view SEM image of $Yb^{3+}$ ions infiltrated into porous silicon Bragg reflector*

The theoretical calculated reflection spectrum is shown in Fig. 3 with thickness $d_H$=105 nm for the high refractive index layer, $n_H$=1.6, thickness $d_L$=131 nm for the low refractive index layer, $n_L$=1.28. If $I_L$ is less than 60 $mA\cdot cm^{-2}$, the porosity is so low that the RE can not infiltrate into porous silicon Bragg reflectors. The difference of the porosity (or the refractive index) will be decreased when the $I_L$ is higher than 60 $mA\cdot cm^{-2}$ and the reflectivity of the band-gap region of Bragg reflectors will be reduced. The porous silicon layers may be electropolished if $I_H$ is higher than 100 $mA\cdot cm^{-2}$ [13].

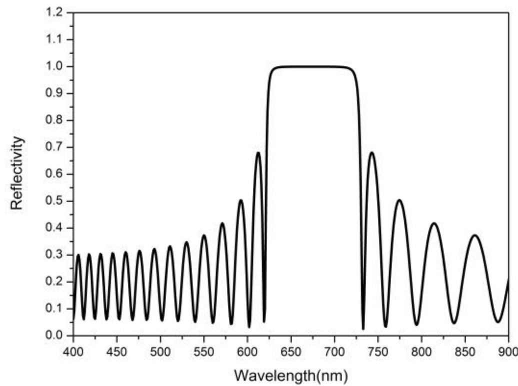


*Fig. 3. Theoretical calculated reflection spectrum of designed porous silicon Bragg reflector*

The rare earth that deposited on the pore walls increase the effective refractive index, i.e., increasing optical thickness leads to the reflection spectrum of porous silicon Bragg reflector redshift. As shown in Fig. 4. The reflection spectrum of the porous silicon Bragg reflector redshifted to 640 nm after doping the rare earth.

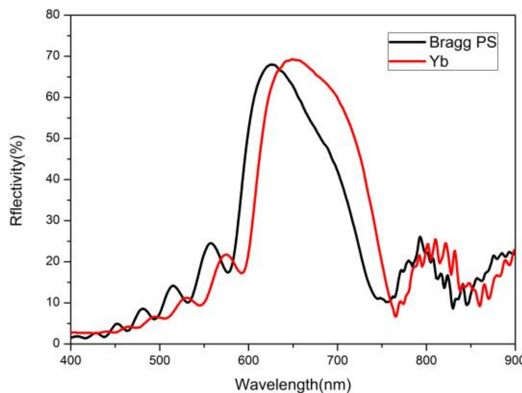


*Fig. 4. Reflection spectrum of porous silicon Bragg reflector(black line), after doping with $Yb^{3+}$ ions(red line)*

Fig. 5 shows the porous silicon fluorescence spectrum with different situations. The porous silicon surface is covered with a layer of $SiO_2$ after the oxygen passivation, and the presence of Si=O bonds is origin of the red PL band from porous silicon [14]. Rare earth dispersed on silicon pillar surface (some rare earth maybe infiltrate into pores) after doping process, and a series of new surface state levels are formed because $Yb^{3+}$ ions levels interact with surface state levels of porous silicon due to the quantum confinement effect. Some of these new levels are higher than former and $Yb^{3+}$ ions can be regarded as carrier trap centers and luminescence centers. The centers capture carriers easily and these captured carriers have a higher probability of optical transitions. Thus, it is possible to enhance the photoluminescence of porous silicon when a suitable concentration of rare earth in PS. The mechanism that enhancement of PS photoluminescence from Yb-doped porous silicon with DBR structures is higher than that from the single-layer porous silicon film: the reflectivity of excitation light is lower because the wavelength of 380 nm is located outside of the band-gap area of the reflection spectrum of porous silicon Bragg reflector, which is conducive to the transmission of excitation light inside the porous silicon DBR structure. The PS fluorescence has the emission band around 620 nm, which is located inside the band-gap of porous silicon Bragg reflector. The DBR structures prevent the upward and the downward fluorescence from transmitting inside porous silicon and reflect the light to surface of the porous silicon. We can observed that: (i) Yb-doped single-layer PS fluorescence is stronger than PS (approximately 1.2 times); (ii) The fluorescence of Yb-doped porous silicon with DBR structures is stronger than the PS with Bragg structures (approximately 2.8 times); (iii) The fluorescence of Yb-doped porous silicon with DBR structures is much higher than single PS (approximately 6.8 times). So we can find that the DBR structures with Yb infiltrated can enhance the PS fluorescence effectively.

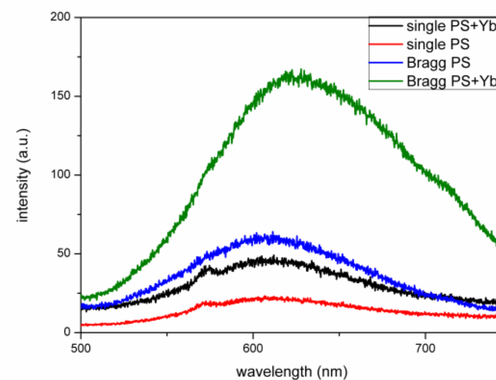


*Fig. 5. Fluorescence spectrum of each sample: fluorescence of single-layer porous silicon film (red line), fluorescence of single-layer porous silicon with $Yb^{3+}$ ions (black line), fluorescence of porous silicon with DBR structures (blue line) and fluorescence of Yb-doped porous silicon with DBR structures (olive line)*

## 4. Conclusions

Doping a suitable concentration of $Yb^{3+}$ ions can enhance the fluorescence of porous silicon. Compared with single-layer porous silicon, the Yb-doped porous silicon with DBR structures can enhance the fluorescence effectively. Rare earth ions and DBR structures double enhanced the porous silicon photoluminescence, which will promote the application of porous silicon.

**Acknowledgement**

This work was supported by the National Science Foundation of China (No. 61265009 and 11264038), Xinjiang Science and Technology Project (No. 201412112).

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