Enhanced photoluminescence from porous silicon microcavities by rare earth doping*

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The photoluminescence (PL) properties of porous silicon microcavities (PSMs) in the visible range at room temperature are improved by doping the rare earth ytterbium (Yb) into PSMs prepared by the electrochemical etching method. It is observed that PSMs doped with the rare earth have an emission band around 630 nm. Compared with the single-layer porous silicon (PS) film, the PSMs doped with Yb have narrower and stronger PL spectrum.

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The wide photoluminescence (PL) band (100—150 nm) and low luminous efficiency[1] of conventional structure porous silicon (PSi) hinder its applications in light-emitting device field. Great efforts have been made in two aspects to solve the problem. The first one is to improve the PL intensity of PSi by making PSi into photonic devices. The porous silicon microcavities (PSMs) can narrow the luminescence bandwidth and enhance the PL intensity compared with single-layer PSi film[2-9]. The second one is to enhance the PL intensity of PSi by doping rare earth (RE) into PSi, resulting in a series of new surface energy levels formed by interaction between RE and PSi[10]. Although there are some reports on improving PL by doping RE into PSMs[11], the influence of doping RE on PL intensity of PSi has not been reported. In this paper, the RE ytterbium (Yb) is doped into PSi with microcavity structures, which results in the enhancement of the PSi PL intensity and the narrower PL bandwidth of PSMs at the same time.

A large difference of refractive indices of the single PSi layers is necessary to obtain high reflectivity mirrors. A highly doped silicon (p^+, 0.03—0.06 Ω·cm^{-1}, <100>) is a good candidate due to the wide range of porosities[12]. Before the corrosion, the monocrystalline silicon must be cleaned in acetone, ethyl alcohol and deionized water by ultrasonic in turn. The solution mixed by hydrofluoric acid (HF 40%) and ethanol (98%) with volume ratio of 1:1 is used as the etchant to anodize the silicon substrate[13], and the current density and the etching time are controlled by computer. The PSMs are composed of a series of PSi films with different refractive indices and thicknesses. Each layer of film satisfies the following relationship as

$$n_H d_H = n_L d_L = \lambda_C/4, \quad (1)$$

$$n_{LC} d_{LC} = m\lambda_C/2, \quad (2)$$

where m is a integer, n_L (n_H) and d_L (d_H) are the refractive index and thickness of the PSi layers with low (high) refractive index, respectively, n_{LC} and d_{LC} are the refractive index and thickness of the microcavity, and λ_C is the resonant mode of PSMs. The PSMs with a resonant mode at 670 nm is designed, because the reflection spectrum will be blue-shifted after oxidation and then red-shifted after doping RE in the PSMs after oxidation. Two Bragg mirrors with 6 periods were obtained by I_H=110 mA·cm^{-2} and I_L=60 mA·cm^{-2}, and the microcavity was formed by I=110 mA·cm^{-2}. The thickness of a sample is 3 000 nm. Then the single layer PSi with the same thickness for comparison was prepared by the current density of 110 mA·cm^{-2}. Finally, all samples were oxidized by immersing in hydrogen peroxide (30%) at 70 °C for 3 h and dried in air.

An RE element we need here has no fluorescence in the visible range. Yb is a good candidate due to its fluorescence in 920—1 100 nm when Yb^{3+} relaxes radiatively from $^2F_{5/2}$ to $^2F_{7/2}$[14]. We dope Yb into PSi by constant-voltage electrochemical doping method[15]. A negatively biased current, relative to a platinum electrode, was applied to the PSi wafer for 5 min under a constant applied voltage of 4 V.

The spectrum of reflection was detected by a spectrophotometer (Hitachi U-4100, Japan). The fluorescence

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spectrum was detected by a fluorescence spectrophotometer (Hitachi F-4600, Japan) with a fixed excitation wavelength of 550 nm, and the emission spectrum was measured in 600—750 nm. Morphology of PSi Bragg reflectors was detected by a ZEISS SUPRA55 VP scanning electronic microscope (SEM).

Fig.1 is the top-view SEM image of Yb-doped PSMs. The pore size is approximately 40 nm. The doped RE is deposited on the surface, the aggregation between different levels occurs, and the particle size ranges from a few nanometers to several hundred nanometers. It is determined by energy dispersive spectroscopy (EDS) analysis that the concentration of Yb^{3+} ions is 2.1%.

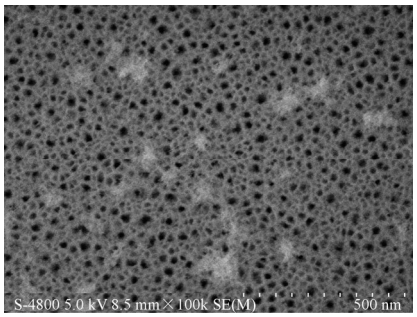

Fig.1 Top-view SEM image of Yb-doped PSMs

Fig.2 shows the cross-sectional view SEM image of PSMs. The structure is composed of two PSi Bragg mirrors sandwiching a PSi film. The dark and light colored PSi films are formed by etching with current densities of 110 mA·cm^{-2} and 60 mA·cm^{-2}, respectively. The thickness of each film of Bragg mirrors is 150 nm, and the thickness of sandwiched PSi film is 560 nm.

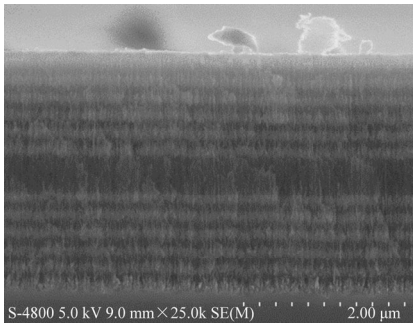

Fig.2 Cross-sectional view SEM image of PSMs

Fig.3 shows the theoretical calculated reflection spectrum of designed PSMs. The high refractive index layer (n_H=1.6) corresponds to d_H=100 nm and I_L=60 mA·cm^{-2}, and the low refractive index layer (n_H=1.14) corresponds to d_L=150 nm and I_H=110 mA·cm^{-2}. The refractive index of center PSi film is 1.14, and the thickness is 595 nm. The reason for choosing this set of current density is that the pore size of each film should be big enough to allow the RE infiltrated, the excessive current density will electropolish the PSi, and a large difference of refractive indices of the single PSi layers should be guaranteed. The reflection spectra of PSMs are shown in Fig.4. The resonant mode of the sample is 670 nm, it moves to 610 nm after oxidation, and it moves to 630 nm after doping RE in the PSMs after oxidation.

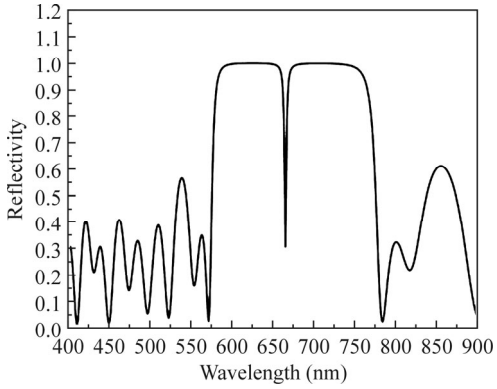

Fig.3 Theoretical calculated reflection spectrum of designed PSMs

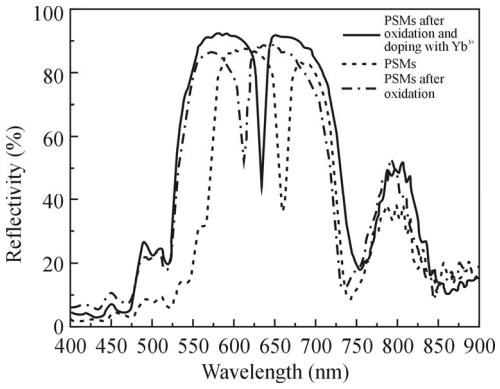

Fig.4 Reflection spectra of PSMs, PSMs after oxidation and PSMs after oxidation and doping with Yb^{3+} ions

Fig.5 shows the fluorescence spectra of PSi with different situations. The single-layer PSi film has no obvious emission peak under the excitation wavelength of 550 nm, and the fluorescence intensity of single-layer PSi film is stronger after doping RE. But the full width at half maximum (*FWHM*) values of the spectra for two single-layer PSi films are both too large, which is about 100 nm. The fluorescence spectrum of PSMs is significantly narrower (≤25 nm) and stronger. The PSM structure is composed of two distributed Bragg reflector (DBR) structures sandwiching a PSi film with high luminescence, which improves the PSi luminescence properties. The high reflective band of PSi-DBR covers the PL spectrum of the microcavity layer, and the resonant mode is suitable for the center of the PL spectrum. Moreover, the enhancement of the fluorescence is attributable to the wavelength which is allowed to be emitted in normal direction. After doping process, Yb^{3+} ions energy levels interact with PSi surface state levels so that a series of new energy levels are formed, the higher energy levels of them can capture carriers easily, and the cap-

tured carriers have a higher probability of optical transitions. Thus, the fluorescence of PSMs is enhanced after doping the RE.

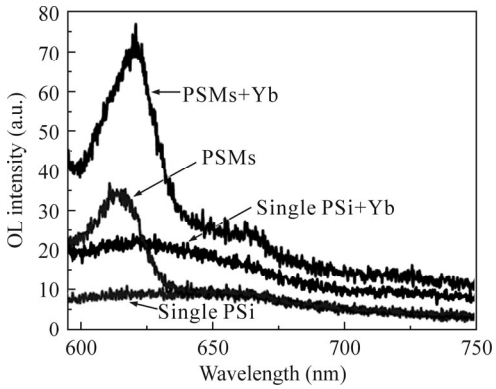

Fig.5 Fluorescence spectra of single-layer PSi film, single-layer PSi doped with Yb^{3+} ions, PSi with microcavity structures and Yb-doped PSi with microcavity structures

We obtain the PSMs by electrochemical etching method, and the FWHM of the PL spectrum is narrow to be 25 nm. The doping of the RE (Yb) enhances the PL intensity. RE and microcavity structures both enhance the PSi PL intensity.

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