JOURNAL OF
Materials
CHEMISTRY

A novel approach for infrared optical activation of neodymium-doped porous silicon using microwave radiation

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Received 27th July 2000, Accepted 23rd October 2000
First published as an Advance Article on the web 5th January 2001

A novel approach for infrared optical activation of neodymium-doped porous silicon (PS:Nd), using microwave radiation, is reported. PS:Nd was prepared using constant-potential electrochemical doping; the effects of microwave heating time, microwave power and the dosage of heat-conducting medium used on the room-temperature photoluminescence (PL) in the infrared region for PS:Nd were investigated. The treated samples emitted intense room-temperature luminescence around 1.06 and 0.90 μm. In addition to thermal activation, the non-thermal interaction of microwave radiation with PS:Nd, mainly resulting in the spread of rare earth and the trapping of oxygen by neodymium ions in the porous layer, is considered to play an important role in the optical activation of neodymium.

Introduction

Porous silicon doped with rare earths (PS:RE) is of considerable interest because of its potential use in optoelectronic devices, such as light-emitting diodes and optical amplifiers. In particular, erbium has attracted the most interest because one of its emission bands at 1.54 μm coincides with the minimum loss wavelength of silica-based optical fibers used in optoelectronics. As a result a tremendous amount of research activity has been devoted to the study of rare earth-doped silicon-based materials for potential use in optoelectronic components.[1] Up to now, different methods, such as electrochemical deposition, diffusion from spin-on films, and ion implantation,[2–4] have been used to incorporate RE into PS. However, owing to the low concentration of the optically active RE in materials prepared by the above methods, infrared optical activation of RE has to be carried out. Infrared optical activation for PS:RE involves changing the doped rare earth atoms to RE^{3+} ions and locating the RE^{3+} ions in a suitable coordination environment, for example, in an RE–O–Si structure,[5] so that the rare earth ions emit their characteristic infrared light when excited with a suitably short wavelength. The traditional activation process uses a high-temperature furnace, in which the annealing temperature usually reaches above 1200 °C and the annealing time is fairly long.[2–4] In some cases, these conditions favour formation of RE–Si, an optically inert structure, and at the same time destroy the quantum confinement structure of PS. In this work we report for the first time the use of microwave radiation to produce neodymium-related luminescence. PS:Nd samples with the highest rare earth concentration so far obtained (10^{21} atoms cm^{-3}) were prepared using constant-potential electrolysis according to our previous work.[6] Intense neodymium-related IR luminescence bands were observed after the microwave radiation treatment. The effects of different treatment conditions, involving microwave heating time, microwave power and the dosage of heat-conducting medium used, on the photoluminescence (PL) of PS:Nd were investigated. The microwave radiation method is demonstrated to be much faster, cleaner, more economical and more effective than conventional heating methods due to the unique interaction between the microwaves and the treated materials.

Experimental

n-Type silicon (n-Si) wafers (purchased from the Semiconductor Processing Company, Germany) with a resistivity of 5–10 Ω cm and a thickness of 0.5 mm were orientated in the ⟨100⟩ plane. Neodymium(III) nitrate hexahydrate (99.9%) was obtained from the Aldrich Chemical Company, Inc., USA and used as received. All other reagents used in this study were of analytical grade. n-Si wafers were anodically etched in a solution composed of hydrofluoric acid (40 wt%) and ethanol in a 1 : 1 volume ratio with a constant current density of 20 mA cm^{-2} for 30 min at room temperature under illumination from two 40 W tungsten lamps set at a constant distance of 15 cm from the sample. After etching, the samples were rinsed with anhydrous ethanol and dried in air at room temperature. A PS wafer was cut into five parts for the same series of Nd-doping experiments. The PS wafer was immersed in an $Nd(NO_3)_3$–acetonitrile solution. A negatively biased current, relative to the platinum electrode, was applied to the PS wafer for 30 min under a constant applied voltage of 4.5 V so that the Nd^{3+} ions were drawn into the pores of PS. The Nd-doped sample was placed in a corundum crucible (20 ml capacity with a 3.7 cm upper diameter) inside a large uncovered tile crucible (150 ml capacity with a 7.2 cm upper diameter). The space between the corundum and the tile crucibles was filled with powdered SiC for conduction of microwave radiation to the sample. Then the tile crucible with sample was placed in an ordinary domestic microwave oven (Model Ms-Z588SDTM, LG Company, Korea) with a microwave frequency of 2450 MHz. Varying heating time, microwave power output and amounts of SiC were used in different experiments. The heated PS:Nd samples were cooled to room temperature in a flow of N_2.

PL emission and excitation spectra were measured using a Spectra-Physics mode-locked Ti–sapphire Tsunami laser as the excitation source, and standard lock-in amplifier techniques. The Ti–sapphire laser was pumped by a visible-frequency cw

DOI: 10.1039/b006080l

laser (Millenia) which provided a power output greater than 5 W at 532 nm. The luminescence signal was dispersed with a monochromator and detected with a Ge detector in the infrared range. The output signals from the lock-in amplifiers were collected and analyzed with a computer. For measuring excitation spectra, the analyzed radiation corresponded to the $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transition of Nd^{3+} ions (~1.06 μm). All the measurements were carried out at room temperature.

Results and discussion

Fig. 1 shows a comparison between the infrared PL spectra of PS:Nd samples irradiated using a constant microwave power (800 W) and SiC packing (150 g) for differing heating times (5, 10, 20, 30, and 60 min) together with the corresponding spectra of an unannealed control sample. The pulsed excitation wavelength is 793 nm. All samples emit intense luminescence around 1.06 and 0.90 μm, which are assigned to the intrashell 4f→4f transitions of Nd^{3+} ions ($^4F_{3/2}\rightarrow{}^4I_{11/2}$ and $^4F_{3/2}\rightarrow{}^4I_{9/2}$, respectively). Obviously, the PL intensity of the samples after annealing is stronger than that of the unannealed control due to the increase in Nd^{3+} ion concentration. The luminescence bands are generally broad, which may be due to various coordination environments for Nd^{3+} ions incorporated in non-crystalline samples. The strong luminescence is thought to be due to the formation of an Nd–O–Si structure. However, the increase in PL intensity with heating time is non-linear, suggesting that there should be an optimum annealing time similar to the behavior observed by Wan and co-workers when investigating different annealing temperatures.[7] We can conclude from Fig. 1B that 30 min is the optimum heating time based on the PL spectra. Wu[8] and Derofeev[9] reported that the RE^{3+} photoluminescence depends on the porosity of the porous silicon, which strongly suggests a correlation between RE^{3+} PL and the PS nanostructures. Further increase in the microwave radiation annealing time probably destroys the quantum confinement structure of the PS:Nd. Broad bands at ~1.06 μm may be relevant to the various Nd centers with different symmetry in PS:Nd.

The excitation spectra (Fig. 1A) monitored at 1.06 μm for the PS:Nd samples showed a similar effect of annealing time on PL to that of the emission spectra. The splitting of the peaks at 0.768 and 0.777 μm for the unannealed sample originated from two different Nd centers in PS. As anodized porous silicon was considered to be composed of silicon nanocrystals, oxidized silicon and/or amorphous silicon,[10] the doped Nd atoms were located in different symmetry fields, and this led to the splitting of the peak. With prolonged annealing time, the split peaks progressively converged to a single peak, which suggests that after microwave treatment the crystal fields for Nd in PS:Nd samples tended to become more uniform. In other words, prolonged microwave treatment produced a single type of luminescence center.

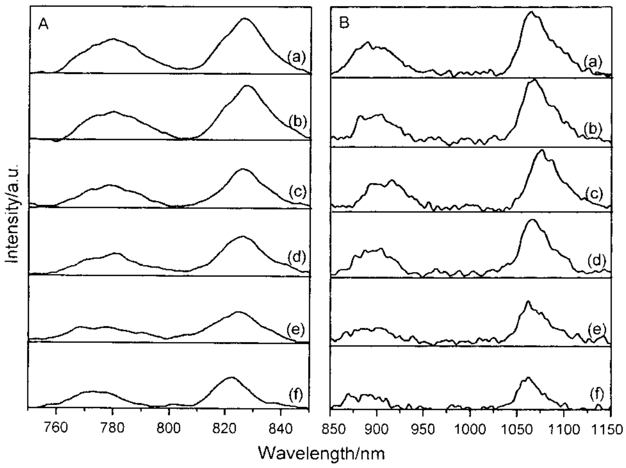

Fig. 1 Infrared excitation (A) and emission (B) spectra for PS:Nd samples annealed for varying times: (a) 60 min, (b) 30 min, (c) 20 min, (d) 10 min, (e) 5 min, and (f) unannealed.

To investigate the crystal fields a comparison of the PL for Nd_2O_3 powder and for PS:Nd after a microwave treatment of 30 min is given in Fig. 2. Both of the emission spectra were roughly similar. This means their luminescence origins were similar, both being due to the formation of coordination environments containing Nd–O bonds. When PS:Nd samples were annealed with microwave radiation in air, oxygen could combine with neodymium giving more neodymium in an optically active trivalent state, thus enhancing the luminescence. But the peak positions were not identical, shifting from 1.06 to 1.08 μm, which indicated that there was some difference between the coordination environments of Nd^{3+} for Nd_2O_3 and PS:Nd. Because of the large bond energy for O–Si (368 kJ mol^{-1})[11] and the high affinity of rare earths for oxygen, speculating upon the formation of Nd–O–Si bands in PS:Nd during the microwave radiation treatment is logical, and the RE–O–Si structure has been demonstrated to be IR active.[5]

Fig. 3 gives a contrast of PL intensities for PS:Nd samples treated with various quantities of heat-conducting material, SiC, (150, 100, 50, 20, and 10 g) with the same microwave power (800 W) and for a constant time (20 min). Similarly to the experiments with varying heating times, the relation between the PL intensity and the quantity of the heat-conducting material used was non-linear. A small quantity of SiC cannot effectively play the role of heat conduction while too much SiC quenches the luminescence since most of the microwaves are used to heat the SiC medium. For a certain microwave radiation annealing process, an appropriate quantity of SiC is necessary. Under the above conditions 100 g of SiC is sufficient.

The effect of microwave power (100, 80, 60, 40, and 20% of 800 W) on the infrared PL intensity of PS:Nd was examined, using a constant quantity of SiC (150 g) and a constant time (20 min). The PL intensity increased greatly with the increase in microwave power, so 100% power of 800 W is suitable for the infrared PL.

An understanding of the microwave interaction with the treated materials has been based on the concepts of dielectric heating and the resonance absorption due to rotational excitation.[12] In fact, microwave heating comes from vibration of the particles (molecules, atoms or ions). In addition to the heating function, the alternating electric field of microwaves obligates the particles to vibrate which accelerates the diffusion of particles inside the material. X-Ray diffraction[13] and electron diffraction measurements[14] indicate that the structure of PS is similar to that of crystalline Si. It can therefore be concluded that silicon atoms essentially do not diffuse, the

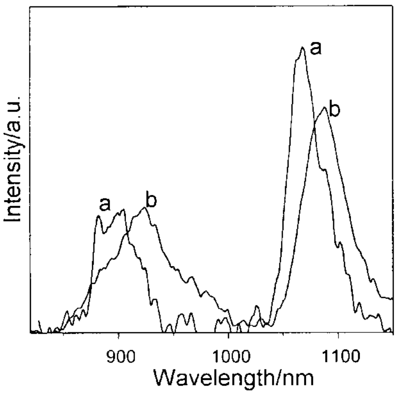

Fig. 2 Infrared emission spectra for (a) PS:Nd sample annealed for 30 min and (b) Nd_2O_3.

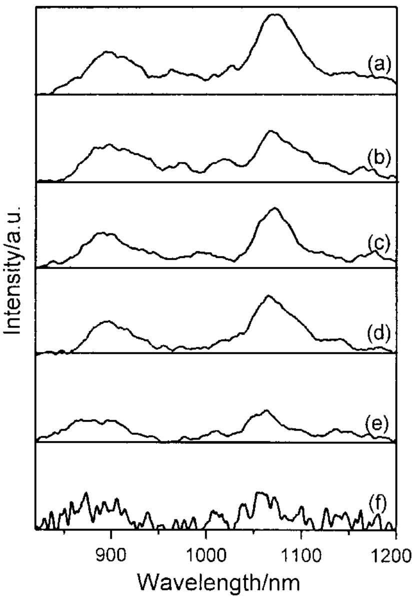

Fig. 3 Infrared emission spectra for PS:Nd samples treated with various quantities of heat-conducting material, SiC: (a) 150 g, (b) 100 g, (c) 50 g, (d) 20 g, (e)10 g, and (f) unannealed.

spread of rare earth atoms being dominant, and it is the doped rare earth in crystalline Si or PS which reacts with trapped oxygen. The diffusion of rare earth on the surface further stimulates the redistribution of oxygen.[15]

Conclusions

In conclusion, based on the high oxygen and rare earth content in matrices obtained by constant-potential electrolysis, a novel approach for the infrared optical activation of neodymium-doped porous silicon (PS:Nd) using microwave radiation is established. Intense room-temperature photoluminescence around 1.06 and 0.90 μm was observed. The influence upon the PL of microwave heating time, microwave power and the quantity of heat-conducting medium added for PS:Nd was investigated, and the optimal conditions were fixed. The mechanism of microwave radiation optical activation for PS:Nd was proposed to be through both thermal activation and the non-thermal interaction of microwave radiation with the treated PS:Nd.

Acknowledgements

This work was financially supported by the Natural Science Foundations of Guangdong Province (grant no. 970163 and 980342) and the State Key Laboratory of Ultrafast Laser Spectroscopy, China.

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