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**Luminescence porous silicon/terbium organic complex hybrid**

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A simple but effective doping method to introduce organometallic complexes into porous silicon was developed. Upon hybridization with a Tb-sulfosalicylic complex, porous silicon emits bright green emission when excited with an UV light. The photoluminescence spectrum shows that only  $Tb^{3+}$  ions emit efficiently while the luminescence of porous silicon and organic ligands are almost thoroughly quenched. Based on the Fourier transform infrared and photoluminescence measurements, it is proposed that  $Tb^{3+}$  complex was physically adsorbed in the pores of porous silicon. The origin of  $Tb^{3+}$  PL was also elucidated from the PL excitation spectrum measurement. © 2000 American Institute of Physics. [S0003-6951(00)00144-3]

Silicon is the most widely used semiconductor in electronic industry. However, with its indirect energy band gap, it is not an ideal semiconductor for photonic applications. Canham<sup>1</sup> has shown that silicon nanostructure such as porous silicon (PS) can have very efficient visible photoluminescence. This was attributed to quantum confinement effect which lifted the energy band gap of silicon from 1.1 eV to about 1.8 eV. By careful control of the etching condition, it is possible to produce porous silicon emitting from red to blue luminescence. Nevertheless, theoretical modeling of silicon nanostructure shows that the band-gap enlargement cannot be accounted for by quantum confinement only.<sup>2-5</sup> Instead, surface states have a profound influence on the luminescence property.<sup>6,7</sup> Various reports have shown that appropriate surface passivation can stabilize and even enhance luminescence: for example, a thin layer of oxide can stabilize the luminescence. When selected organic complexes are chemically bonded to the silicon at the surface, the luminescence property of PS may be altered. The most common consequent is the quenching of the luminescence. Buriak<sup>8</sup> has reported suitable organic complexes which offers a variety of luminescence and photochemical properties. Selective emission or absorption can open up applications not only in optoelectronics but also photolithographic processes in integrated circuits. In this work, we report a simple but effective method to deposit an organometallic complex, Tb-sulfosalicylic complex into the PS. Strong  $Tb^{3+}$  emission was observed. Our investigation showed that this could be an efficient way to deposit rare earth metals into PS.

Solution of Tb-sulfosalicylic complex (Tbssal) was made by mixing aqueous solution of  $Tb(NO_3)_3 \cdot 6H_2O$  with

that of 5-sulfosalicylic acid in the ratio of Tb:sulfosalicylic = 1:3. The concentration for Tb(III) was 0.15 mol/l and pH was adjusted to 8 with 0.1 M NaOH. The Si wafers used were p-type (100) with resistivity of 6–9  $\Omega$  cm. PS samples were prepared by anodizing the Si wafers in a HF(48%) and ethanol mixture (1:1). The etching time was 30 min and the current density was 15 mA/cm<sup>2</sup>. A 50 W tungsten lamp was used for illumination during anodization. Hybridization was performed by simply immersing the PS into a solution of Tbssal complex, standing at room temperature for 3–24 h, then rinsing with excess deionized water and blown dry for photoluminescence (PL) and Fourier transform infrared spectroscopy (FTIR) measurements.

For PL measurements, the 325 nm line of a He–Cd laser was used as an excitation source, while for PL excitation (PLE) spectrum measurement, a 1 kW xenon arc lamp was used. The luminescence spectrum was analyzed by a 0.25 m focal length double monochromator with a Peltier cooled photomultiplier tube and processed with a lock-in amplifier. A Nicolet Magna 550 Series II FTIR spectrometer was used to record IR absorption spectrum in transmission mode.

Figure 1 shows the PL spectrum of PS before and after immersion in Tbssal complex solution. Untreated PS has a broad PL spectrum peaked at ~650 nm. After immersion in Tbssal complex solution, the broad PL of PS was gradually quenched, and four narrow bands centered at 488, 544, 580, and 620 nm appeared. These bands were identified as the characteristic  $^3D_4 \rightarrow ^7F_J$  (where  $J=3,4,5,6$ ) transition of  $Tb^{3+}$  ions, which indicate that  $Tb^{3+}$  ions are present in the PS. Correlation between PL band of  $Tb^{3+}$  and that of PS was also observed in Fig. 1. An increase of  $Tb^{3+}$  PL was accompanied by a decrease of the PS PL. This shows that presence of  $Tb^{3+}$  contributed to PL quenching of PS and the two processes are linked.

When PS was directly blown dry without further wash-

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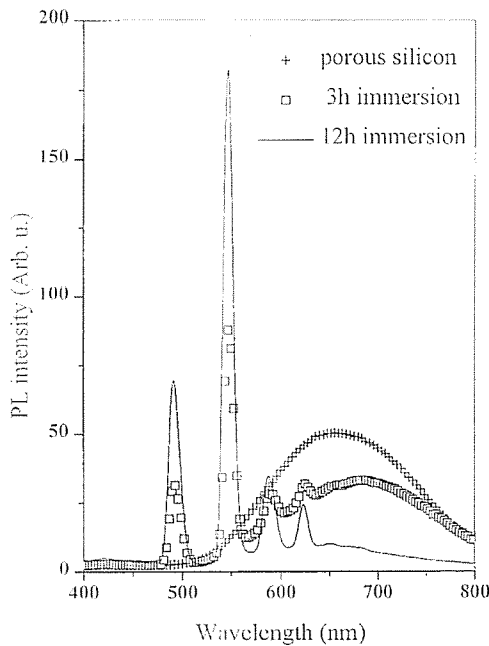


FIG. 1. Fluorescence of hybridized PS.

ing with excess water after immersion, the shape of the PL spectrum was similar to that of Tbssal complex (Fig. 2). Both spectra consist of a broad band centered at 418 nm for the organic ligands and four narrow bands for  $Tb^{3+}$  ions, while the broad band was almost thoroughly quenched for hybridized and washed PS (Fig. 1). The PL of the hybridized samples was checked again for any degradation after three months, and it was found that the emission from  $Tb^{3+}$  ions remained as strong as before. This indicates that there was no degradation of either the Tbssal or PS.

Figure 3(a) is the FTIR spectrum of Tbssal complex. Characteristic vibration peaks for Tbssal complex were found at  $\sim 3500$ , 2917, 1745, 1163, 898, and  $674\text{ cm}^{-1}$ . All

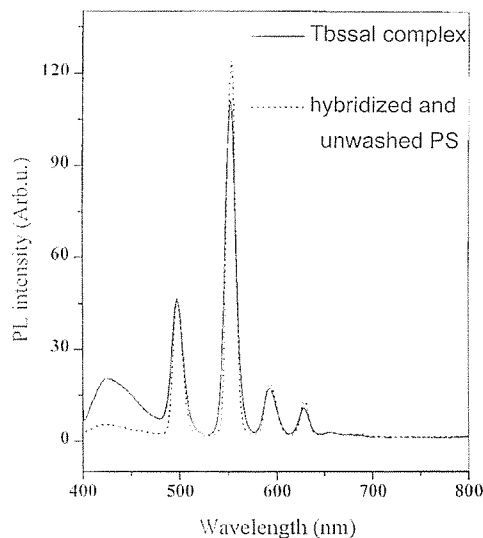


FIG. 2. PL spectra of Tbssal complex and hybridized and unwashed PS.

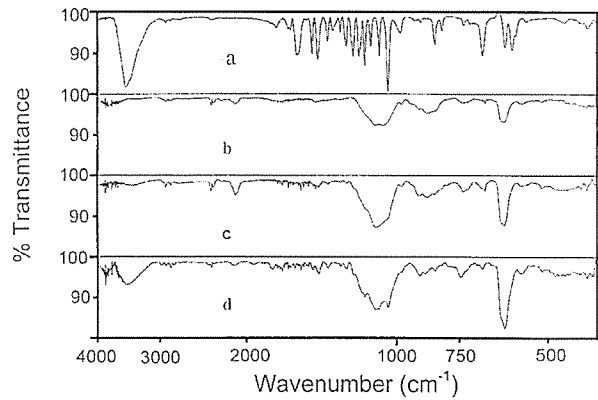


FIG. 3. FTIR spectra of hybridized PS. (a) Tbssal complex; (b) PS before hybridization; (c) 3 h hybridization; (d) 12 h hybridization.

these peaks grow with immersion time, as shown in Figs. 3(c) and 3(d), which means that more Tbssal complex was gradually adsorbed on the surface of silicon. These results are consistent with that of the PL measurements in Fig. 1. There are also some changes on intensity of the characteristic vibration peaks for PS, but the change are smaller than that for the Tbssal complex and is less informative because of uncertainty of FTIR intensity. The Si-H bond can be considered as the most chemically active parts in PS. However, peaks corresponding to the vibration of Si-H bond at  $2110$  and  $622\text{ cm}^{-1}$  did not decrease apparently even after 24 h immersion. This phenomenon supports that there was no chemical reaction between Tbssal complex and the surface of PS. Figures 1 and 2 show that after hybridization, the fluorescence of  $Tb^{3+}$  was observed, while those of both organic ligands and PS were greatly quenched. To elucidate the origin of the  $Tb^{3+}$  PL, PL excitation spectrum was measured as shown in Fig. 4. Excitation spectrum of  $Tb^{3+}$  hybridized on PS gives a broad band peaked at 350 nm, and this spectrum is different from that of direct  $Tb^{3+}$  excitation as in the case of EDTA complex of  $Tb^{3+}$  (Ref. 9). Excitation spectrum of  $Tb^{3+}$  in Tbssal complex was peaked at 370 nm with a shoulder at 330–350 nm. This excitation spectrum is considered as due to UV light being absorbed by organic ligands, which transfer part of the energy to  $Tb^{3+}$  ions, which then emit its

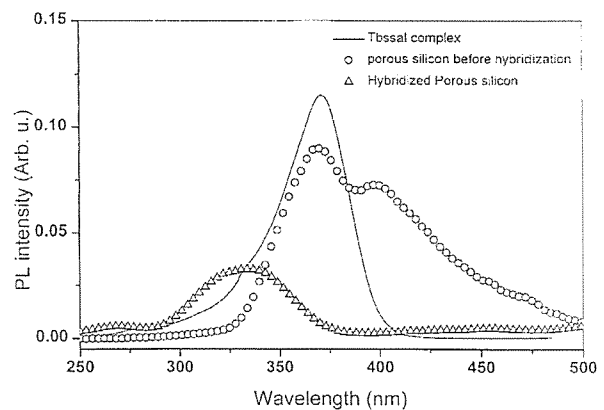


FIG. 4. PL excitation spectra of Tbssal complex and PS before and after hybridization.

characteristic fluorescence.<sup>9</sup> The organic ligands also emit via its  $S_1 \rightarrow S_0$  transition (where  $S_0$  and  $S_1$  are the ground and excited singlet state, respectively), and give the broad band peaked at 418 nm as shown in Fig. 2. However, the PL excitation spectrum of hybridized PS has a distinct blueshift with respect to Tbssal complex, and the excitation strength dropped markedly, whereas, the excitation spectrum of PS has a 370 nm peak (Fig. 4).

Tbssal complex consists of  $Tb^{3+}$  ions surrounded by sulfosalicylates which contain sulfonic, carboxylate, and hydroxyl groups. Since all these groups are chemically inert, it is unlikely that the presence of  $Tb^{3+}$  ions is a consequence of a chemical reaction. As PS has long and narrow pores, there are two possible mechanisms for the  $Tb^{3+}$  fluorescence. When PS is immersed in Tbssal complex solution, its pores will be filled up with solution containing Tbssal complex. These Tbssal complex molecules may be adsorbed on the surface of silicon or in the solution that is trapped in the pores, and both could give  $Tb^{3+}$  fluorescence. However, the former mechanism is most likely since PL quenching process of PS is rather slow. It took about 3 h for half quenching and about 12 h for thoroughly quenching, and it is unreasonable for quenching by trapped solution to take such a long time. It is believed that broad band at 418 nm in Fig. 2 originated from the latter mechanism, and these Tbssal complex molecules in solution could be washed away but there were still some Tbssal complex molecules remained on the surface of PS and could not be removed by simply washing. Other evidence also favors the former mechanism. Some samples were subjected to ultrasonic washing in excess water, but no significant difference was found on PL measurements. Evidence from FTIR also appreciates that Tbssal complexes are adsorbed on the silicon surface.

An energy diagram shown in Fig. 5 is proposed for the energy transfer process of the hybridized PS. As the lowest singlet excited state of organic ligands,  $S_1$ , overlap with the excited state of PS, most of the energy in  $S_1$  will be transferred to PS and thus fluorescence of organic ligands is quenched. Excited state of PS could also relax via vibration states of organic ligands and this would effectively quench the PS PL. However, when excited with shorter wavelength UV light, organic ligands can be excited to higher excited state, such as  $S_2$ ,  $S_3$ , etc. These states will relax via two ways: (1) relax to its  $S_1$  state and then excited states of PS; (2) transfer the energy to its triplet excited states, and then the excited state of  $Tb^{3+}$ , which then emit fluorescence. In

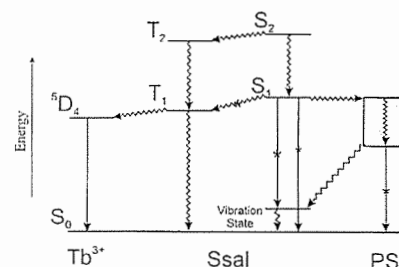


FIG. 5. A proposed energy transfer process in PS hybridized with Tbssal complex. (\*) process insignificant after hybridization.

the hybridized PS, it is the latter mechanism that was observed.

In summary, a novel method has been developed to hybridize  $Tb^{3+}$  ions onto PS through immersion of PS in a solution that contains  $Tb^{3+}$  complex. The PL and FTIR results show that no chemical reaction took place during immersion, and instead, a physical adsorption occurred in which Tbssal was adsorbed onto the PS surface. The adsorption quenched the PS PL, and a strong  $4f$  intrashell transition of  $Tb^{3+}$  was observed. From the results of PL excitation spectrum, a luminescence mechanism is proposed. No degradation in the luminescence was detected after leaving the samples in ambient environment with humidity varied from 50% to 95% over a period of three months. This demonstrates convincingly the high stability of the hybridized samples. The result can be potentially applied to prepare metalorganic/silicon materials. The stability of the adsorption process means that it is possible to introduce various luminescence organic complexes into porous silicon, and hence a tunable emission process, which is simple and straightforward can be made available. Such hybridized PS has potential application in sensor, and indicator area.

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<sup>1</sup>L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).

<sup>2</sup>J.-B. Xia and K. W. Cheah, *Phys. Rev. B* **55**, 15688 (1997).

<sup>3</sup>B. Delley and E. F. Steigmeier, *Phys. Rev. B* **47**, 1397 (1993).

<sup>4</sup>J.-B. Xia and Y. C. Chang, *Phys. Rev. B* **48**, 5179 (1993).

<sup>5</sup>F. Buda, J. Kohanoff, and M. Parrinello, *Phys. Rev. Lett.* **69**, 1272 (1992).

<sup>6</sup>K. W. Cheah, L. C. Ho, J.-B. Xia, J. Li, W. H. Zheng, W. R. Zhuang, and Q. M. Wang, *Appl. Phys. A: Mater. Sci. Process.* **60**, 601 (1995).

<sup>7</sup>J.-B. Xia and K. W. Cheah, *Phys. Rev. B* **59**, 14876 (1999).

<sup>8</sup>J. M. Buriak, *Chem. Commun.* 1051 (1999).

<sup>9</sup>W. D. Horrocks, Jr. and M. Albin, *Progress in Inorganic Chemistry*, edited by S. J. Lippard (Wiley, New York, 1984), Vol. 31, pp. 1-104.