New Insight on the Luminescence Mechanism of Light-Emitting Porous Silicon

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The observations of efficient infrared up-conversion luminescence and its anisotropic behaviour verify that the PS sample is an assembly of quantum confined structures. A double-resonance enhanced third-order nonlinear optical process is suggested to interpret the experimental observation. Based on the carrier transfer mechanism involved in the light emission process studied by the picosecond time-resolved luminescence spectroscopy, a comprehensive luminescence model is proposed. A tight-binding calculation shows that the luminescence peak positions could only appear at a series of discrete energies. This "pinning" phenomenon is proved experimentally.

1. Introduction

The discovery of visible light emission from highly porous silicon (PS) by Canham[1] has generated a great deal of interest. One of the key problems which attracts the attention of many researchers is the mechanism involved in luminescence. In this paper, we are seeking some new experimental approaches which provide further evidences in confirmatively supporting the quantum confinement mechanism while the roles played by the surface states are also included. A comprehensive luminescence model which takes account of the carrier transfer processes between the confined states and the surface states is proposed.

2. Sample Preparation

The substrates used in this work were all p-type Si wafers with resistivity of 10 $\Omega \cdot$cm mostly. The anodic etching was carried out in a solution of HF: ethanol=1:1 or HF: H_2O=1:1 at constant current density between 5–30 mA/cm² at room temperature and under the natural light illumination. Some sorts of post anodic treatments were occasionally used.

3. Evidences of Quantum Confinement

3.1 Infrared up-conversion luminescence[2]

The infrared up-conversion luminescence was excited by a passively mode-locked amplified Nd-doped YAG laser emitting 50 ps pulses at 1.06 μm. The spectrum of a PS sample is shown in Fig.1. It consists of a broad PL band centered at 590 nm with a

FWHM of ~100 nm and a relatively small sharp peak at 355 nm.
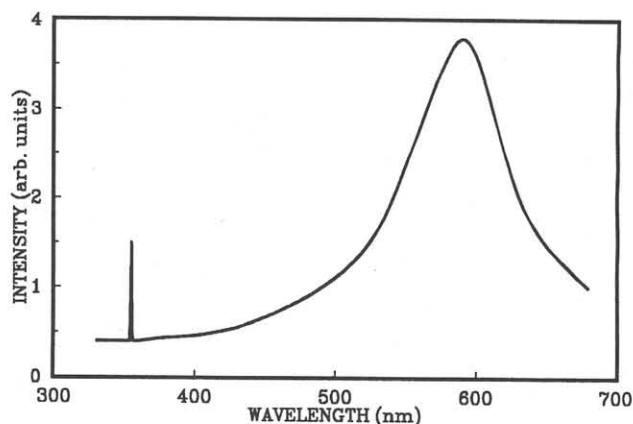

Fig.1   IR up-conversion spectrum of porous silicon.

The UV excited PL spectrum of the PS sample was also recorded by a 355 nm Q-switched laser. The spectrum coincides fairly well with the up-conversion spectrum. It is thus verified that the radiative de-excitation processes involved in the UV-excited PL and IR-excited up-conversion luminescence are actually the same, although their excitation processes are different.

The dependence of up-conversion luminescence intensity I on pump power P was measured. A linear relation between I and P^3 was observed, which coincides with the relation of a typical third-order nonlinear optical process.

We suggest that the IR up-conversion luminescence consists of two processes. The first one is a double-resonance enhanced third-harmonic generation process. The triple of the incident photon

energy approaches the energy difference between a upper level and a fundamental level. In addition, there exists a middle level which arises most possibly due to the quantum confinement. A two-photon resonance due to the presence of middle level greatly enhances the THG in PS. The second process is similar to the light-emission process of PS excited by external UV light. The signal of the enhanced THG in PS could act as an internal pump source to excite visible-light emission just as the UV light does.

3.2 Anisotropic nonlinear susceptibility[3]

It is found that the up-conversion luminescence efficiency of PS is anisotropic as the polarization vector of normally incident fundamental light is rotated. The result is shown in Fig.2. The up-conversion
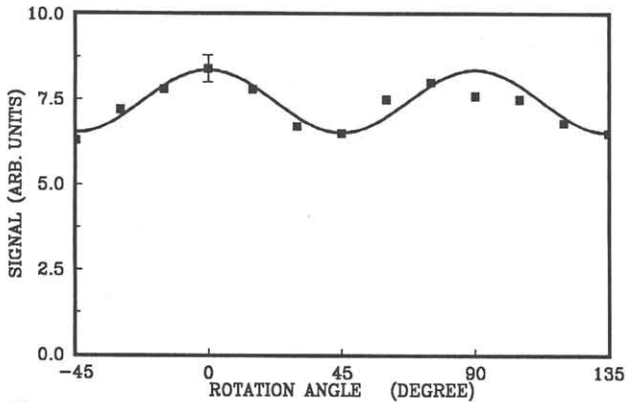
Fig.2   Up-conversion signal intensity as a functions of rotation angle.

luminescence efficiency of PS shows the same fourfold symmetry and almost the same modulation depth but a phase difference of π as that of the THG efficiency of c-Si. These results demonstrate that PS has a strong crystalline anisotropic behavior and a different nonlinear optical response from that of c-Si. As it is known[4] that if silicon is changed from crystalline to non-crystalline, the only difference between the curve of THG efficiency versus crystal orientation is the reduction of modulation depth rather than the change of phase. For a-Si, the modulation depth would be zero.

4. Exciton Dynamics

4.1 Carrier transfer mechanism

We performed the picosecond time-resolved PL measurements in the temperature range of 77K to 410K. Fig. 3 shows the room temperature time-resolved PL spectra which consist of two bands centered at the wavelengths of ~615 nm and 700 nm (denoted as band E and S) respectively. The higher energy peak (band E) does not contribute to the steady emission process as this peak does not appear in the

ordinary PL spectrum. Meanwhile, it is also shown that the intensity of band E decays faster than that of band S. The S band in our case is most possibly originated from surface states since its peak position is strongly affected by the post anodic treatment. The S band here seems coincide with the slow band in Koch's experiment[5]. But we do not think it comes from the recombination process involving two surface states as
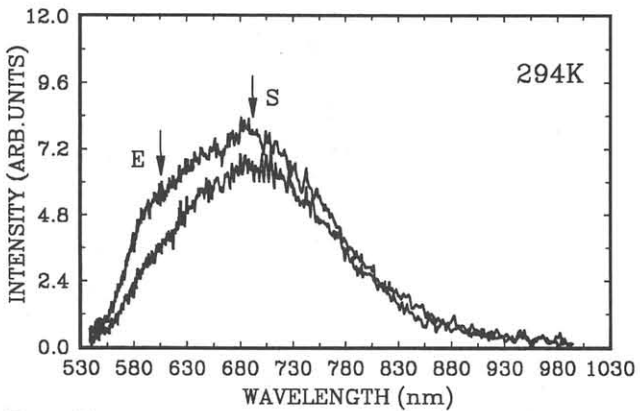
Fig.3 Picosecond time-resolved PL spectra taken at 100ps(upper curve) and 1.5ns(lower curve) after the light excitation.

Koch et al. proposed. We propose that the mechanism of S band is the recombination of localized electrons trapped by the surface states locating within the band gap of PS with its partner in the valence band.

It is not unreasonable to assign the E band to the emission from confined exciton states in PS quantum wires or dots. The temperature dependence of its luminescence intensity coincides qualitatively with the behavior of excitons.

To understand the carrier transfer dynamics between the quantum confined exciton states and the localized surface states, the luminescence intensities
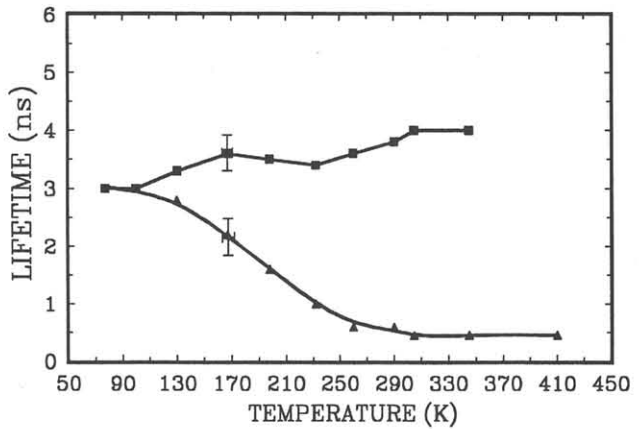
Fig.4 Temperature dependencies of $\tau_e(\blacksquare)$ and $\tau_t(\blacktriangle)$

integrated in the spectral width between wavelengths 580 nm and 630 nm as a function of time for different temperatures were measured. In general, the luminescence intensity follows a nonexponential decay,

which can be described by two exponential processes, i.e., a faster decay at the beginning with a lifetime of τ_t, and then followed by a slower decay with a lifetime of τ_e. The temperature-dependencies of τ_t and τ_e are shown in Fig.4. τ_e is nearly independent on temperature, which is consistent with a geometrically confined exciton decay model[6]. However, τ_t is strongly temperature dependent. At temperatures below 100K, there is no faster decay at the beginning. The excited carriers mainly populate in the quantum confined exciton states E. In the temperature range of 100K to 260K, τ_t decreases dramatically. The nonradiative transfer of quantum confined excitons into the localized surface states is thermally activated. At temperatures above 260K, τ_t is much shorter than τ_e. The excited carriers are mostly transferred from the quantum confined exciton states into localized surface states. It is therefore only the de-excitation of carriers in the latter states contributes to the room-temperature steady PL spectra.

4.2 Comprehensive luminescence model

Based on the above results, a comprehensive luminescence mechanism of light-emitting PS could be proposed. The photon-excited electron-hole pairs are first trapped in the crystalline Si nanostructures as confined excitons. They are then radiatively relaxed into ground state through two possible channels. One is the direct radiative recombination which occurs with a time constant of several ns. Another is that the confined excitons are first non-radiatively transferring into surface localized states through a thermal activation process, and then radiatively relax into ground state, resulting in the ordinary steady PL signal. Once the temperature is high enough that τ_t is shorter than the lifetime of confined excitons, τ_e, then the second channel dominates the radiative recombination process. It is thus believed that the quantum confinement is the necessary condition for visible light emission of PS, while the steady state PL spectrum is directly related with the surface states.

5. Band Gap Widening and "Pinning" of Luminescence Peaks

The band gap widening of PS was calculated based on the quantum-size-effect model by simulating the PS as an assembly of silicon dots[7]. A spherical shaped cluster with all the Si atoms located at the sites of a diamond-lattice and with one Si atom sitting at the center has been used as the model.

The energy gap E_g as a function of the dimension of the cluster was calculated by using tight-binding method. If the cluster could only exist in the close-shelled form, E_g could only take a series of discrete
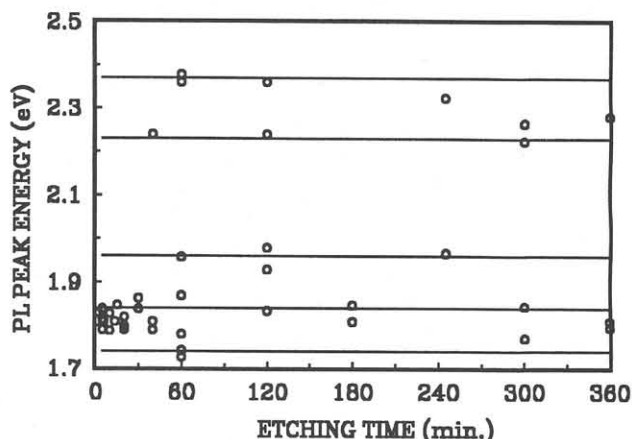

Fig.5 PL peak energies from different PS samples. The "pinning" effect is explained by the quantum confinement mechanism.

values. Correspondingly, the PL peak positions would appear at or near some discrete energies. This is described as a "pinning" effect.

To check the validity of the above theoretical prediction, more than 30 PS samples prepared at different anodic etching times have been measured and their PL peaks are positioned at or near some discrete energies as shown in Fig.5. The pinning energies E_P are 2.37, 2.23, 1.96, 1.84 and 1.74 eV respectively. By considering the energy difference between the band edge and the surface state, the later is believed in response to the PL peak, the agreement between the experimental pinning energies and the calculated band gap energies is satisfactory.

References

1. L. T. Canham, *Appl. Phys. Lett.* **57**(1990) 1046.
2. Jian Wang, Hong-bing Jiang, Weng-cheng Wang, Jia-biao Zheng, Fu-long Zhang, Ping-hai Hao, Xiao-yuan Hou and Xun Wang, *Phys. Rev. Lett.* **69**(1992) 3252.
3. Jian Wang, Hong-bing Jiang, Wen-cheng Wang, Jia-biao Zheng, Fu-long Zhang, Ping-hai Hao, Xiao-yuan Hou and Xun Wang, *Phys. Rev.* **B** (to appear).
4. D.J. Moss, H.M. Van Driel and J.E. Sipe, *Appl. Phys. Lett.* **48**(1986) 1150.
5. F. Koch, V. Petrova-Koch, T. Muschik, A. Nikolov and V. Gavrilenko, *MRS Sym. Proc.* Vol. 283(1993) 197.
6. M. Kohl, D. Heitmann, W.W. Ruhle, P. Grambow and K. Ploog, *Phys. Rev.* **B41**(1990) 12338.
7. Fu Huaxiang, Ye Ling and Xie Xide, *Phys. Rev.* **B** (to appear).