Pinning of Photoluminescence Peak Positions for Light-Emitting Porous Silicon: An Evidence of Quantum Size Effect

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In the present work energies of photoluminescent (PL) peaks of porous Si were measured on as-etched samples. It was found that the PL peak energies occur only at or nearly at a series of discrete values and exhibit a "pinning" characteristic. A tight-binding calculation was carried out to study the variation of gap energies of Si nanostructures with the size of the clusters. If Si clusters took stable forms of closed shells with their sizes in the range of 1–2 nm, the change of gap energies gave obvious discontinuity. Good agreement was found between the "pinning" energies of PL and the energy gaps of subsequent closed-shell Si clusters. This might be considered as evidence for the quantum size effect of porous Si.

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The discovery of visible light emission from highly porous silicon (PS) by Canham [1] has generated a great deal of interest because of its potential applications in optical interconnection and display technology. One of the key problems which attracts the attention of many researchers is the mechanism involved in luminescence. Although a variety of possible models have been proposed [2–5], it is now agreed upon by most works that the quantum size effect in the spongelike PS skeleton might play a key role in its optical properties as suggested originally by Canham. In addition, the surface states or surface related species are found also to be responsible for the luminescence process [5]. Many experiments have been devoted to seeking evidences for supporting the quantum-size-effect model. The most convincing fact is the relation between the blueshift of the luminescence peak and the porosity which really represents the average size of the Si nanostructures. Theoretically the quantum-size-effect model is the model for which most calculations have been made. Some authors modeled porous silicon as an assembly of silicon wires [6–9], others used a dot or cluster model to simulate the PS skeleton [10–13]. In our previous paper [14], a spherical shaped cluster is used to simulate the Si nanostructure. The absorption coefficient or dielectric function and band gaps for different sizes of clusters are calculated. In the present work, additional results on the size dependence of the gap energy will be presented. It is found that the calculated energy gaps of Si nanostructures do not vary continuously if Si atoms in clusters could only form closed shell structures. It is thus expected that the experimentally observed luminescence peaks will appear only at a series of discrete energies, if the quantum confinement was the predominant mechanism involved in the luminescence process. The discreteness of luminescence peaks is proved to be quite distinguishable in the experimental observation.

It is now commonly agreed upon that the structure of PS is spongelike; i.e., it consists of wires and/or dots with nonuniform dimensions. Even if the PS skeleton is wirelike, photoexcited carriers in a corrugated wire would populate mostly in thicker areas, where energy gaps are narrower than that of the surrounding thinner areas. Therefore, it seems more reasonable to simulate the PS nanostructures by an assembly of clusters rather than by rods. 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 lattice constant in the clusters is taken as that of bulk Si (5.43 Å) and all the dangling bonds of atoms in the outer shells of the cluster are saturated with hydrogen atoms with Si-H bond length taken as 1.48 Å. The calculation of the energy gap has been carried out by using the tight-binding method (TB). The TB model of Vogl, Hjalmarson, and Dow [15] has been adopted with the orbital interaction parameters modified according to Yamaguchi [16]. To evaluate the accuracy of the calculation, the band gap value obtained with periodic boundary conditions is derived by the above method, and the value of 0.8 eV is obtained, which is somewhat closer to the known band gap of bulk Si than a previous calculation [13].

The calculated energy gap E_g as a function of the dimension D of the cluster is shown in Fig. 1. The number of equivalent atoms on each shell, the total number of atoms in the cluster, the corresponding diameter of the cluster and its energy gap obtained from the interpolation of Fig. 1 are listed in Table I. It can be seen that for small clusters, the energy gap $E_g \sim D$ curve has a larger slope than that for larger clusters. At the same time, the size difference between successive shells is more significant for small clusters. It is not unreasonable to assume that the clusters with closed outermost shells might be more stable than open shell clusters.

According to Table I, the energy difference between two subsequent discrete energy gaps in the range of 1.8–3.0 eV (i.e., visible range) is in the order of 0.1 eV, which is detectable within the precision limit of the pho-

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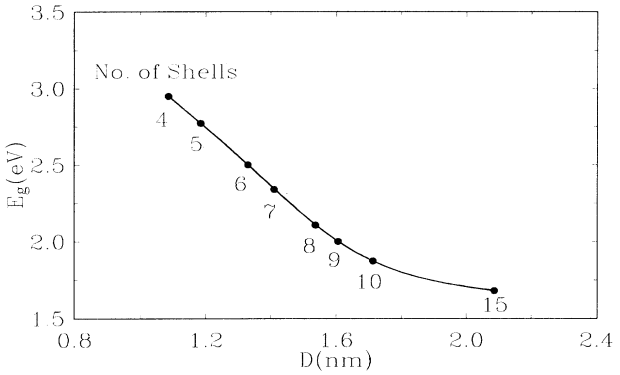

FIG. 1. Energy gap (E_g) versus the diameter of the cluster. Number of Si shells in the cluster are indicated by the dots on the curve.

toluminescence (PL) measurement. To check the validity of the above theoretical prediction, measurements for a number of luminescent PS samples have been made The data are shown in Fig. 2.

All samples were prepared with p-type Si(100) single crystal wafers of different resistivities. The anodic etching was carried out in a solution of 48% HF: ethonal=1:1 with the anodic current density of several mA/cm^2. The etching time varied from several minutes to several hours. All PL measurements were taken on as-etched samples without any post anodic treatment. It is believed that the internal surface of these PS samples are H terminated, which agrees well with the cluster model used in our calculation. The 457.9 nm line of an Ar^+ laser was used as the light source in PL measurements with the laser power of 1–10 mW and the beam diameter on the sample larger than 200 μm. The luminescence spectra were recorded by a Jobin-Yvon U1000 Spectrometer with 1800 g/mm holographic gratings and cooled photomultiplier/GaAs detector. All the measurements were performed at room temperature.

More than 30 PS samples prepared with various anodic etching times were measured and it was found that all PL peaks were at or nearly at certain discrete energies shown by the horizontal lines in Fig. 2. The phenomenon was defined here as a "pinning" effect, with pinning energies E lying at 2.37, 2.23, 1.96, 1.84, and 1.74 eV, respectively. By comparing these values with the series of discrete gap energies in Table I, i.e., E_g=2.50, 2.33, 2.09, 2.01, and 1.86 eV for the number of shells equal to 6, 7, 8, 9, and 10, respectively, the energy difference $\Delta E = E_g - E_p$ with values of 0.13, 0.10, 0.13, 0.17, and 0.12 eV can be obtained. The average value of ΔE is 0.13 ± 0.05 eV. In principle, it is not expected that the luminescent photon energy should be the same as that of the band gap energy. It has been proposed that the steady state PL at room temperature is mainly contributed by the radiative recombination of carriers in the surface localized states [17]. In a picosecond time-resolved PL study, it was found that the energy level of surface states for hydrogen-terminated PS is about 0.15 eV below that of confined excitons in PS cores [18], the latter was estimated to be 0.3–0.4 eV below the lowest conduction band level [9]. Therefore, the pinning energies must be about 0.45 eV smaller than that of corresponding gap energies. The E value of 0.13 eV derived above seems to be too small. The discrepancy might be due to a systematic error in theoretical calculation. Since the energy gap of bulk Si obtained from the present calculation is underestimated by a value of 0.3 eV. If the theoretical curve in Fig. 1 could be shifted upward by an energy of 0.3 eV, the agreement between the pinning energy and the band gap would be perfect. Although this agreement might be somewhat fortuitous, however, the present result might illustrate qualitatively that the pinning phenomenon could be true and the origin of PL might be due to quantum confinement.

Recently, Zhang *et al.* [19] reported a steplike behavior in the relationship of PL peak energy versus HF con-

TABLE I. For different cluster models, the number of equivalent atoms on each shell, the total number of atoms in the cluster, the corresponding diameter of the cluster and its energy gap value obtained from Fig. 1 are listed.

Order of shells	Number of equivalent atoms on the shell	Accumulated number of atoms in the cluster	Diameter of the cluster (Å)	Value of energy gap (eV)
1	4	5	4.70	
2	12	17	7.68	
3	12	29	9.01	
4	6	35	10.86	2.95
5	12	47	11.83	2.78
6	24	71	13.30	2.50
7	12 and 4	87	14.11	2.33
8	12	99	15.36	2.09
9	24	123	16.06	2.01
10	24	147	17.17	1.86
15	24	239	20.85	1.68

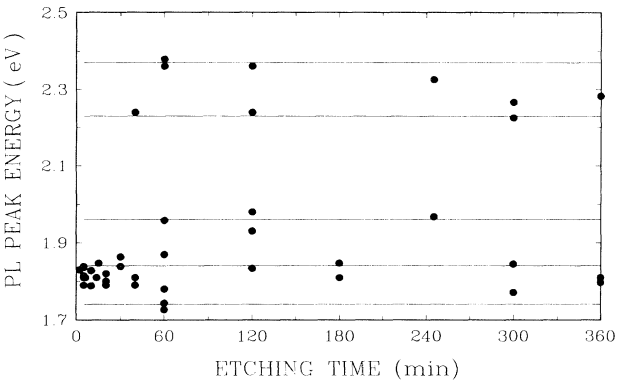

FIG. 2. The energies of photoluminescent peaks measured on different as-etched porous silicon samples are pinned at or near some discrete energies (horizontal lines).

centration for *p*-type PS. A formation mechanism of PS cores with discrete dimensions was postulated. Their observed PL peaks at 1.84 eV, 1.96 eV, and 2.31 eV agree with our measurements, whereas the two pinning energies at 1.74 and 2.23 eV predicted by our theoretical calculation did not exist in their experiment. Their argument that the step between the 2.31 and 1.96 eV peaks was due to the fact that one more layer of atoms from the PS cores was etched away did not seem to be plausible, since it was based on the assumption that the PL peak energy should be exactly equal to the energy gap of PS. Nevertheless, their experimental observation also partially supports our theoretical model.

It is noteworthy that not all the PL peaks of PS samples are pinned at the above energy positions. The postanodic treatment such as oxidation will partially destroy the outermost closed shell of Si clusters; as a result the PL peak energies would shift from the above pinning values. Although, the assumption that all clusters in PS are closed shelled might not be true, it is reasonable to anticipate that during the anodic etching, a major portion of Si clusters are in the form of closed shell, whereas the rest are not. This might explain the appearance of a wide luminescence peak for all light-emitting PS samples.

As a conclusion, from the theoretical calculation it was predicted that the gap energy of Si nanostructures did not change continuously if Si clusters were assumed to exist in the stable form of closed shells with their sizes in the range of 1–2 nm. As a consequence, the luminescence peak energy of PS should also appear at a series of discrete values. This pinning characteristic was observed experimentally by measurements performed on as-etched PS samples. The observed peaks did support the quantum size effect in the light emitting PS.

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