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Optical absorption property of oxidized free-standing porous silicon films*

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Abstract: We have systematically studied the evolution of the optical absorption of free-standing PS films during thermal oxidation at 200 °C in air. Our experiment results show the evolution of transmission curve is quite complicated, which red-shifts first and then blue-shifts during thermal oxidation. At the same time, the transmission at the low energy decreases first and then increases. We propose an explanation as follows: (1) the energy gap associated with each crystallite should increase during thermal oxidation process, due to the quantum confinement effect; (2) the energy gap should decrease with an increase in oxygen termination atoms. Both the increasing of the gap due to the quantum confinement effect and the decreasing of the gap due to the Si–O bond formation cause a complicated evolution of optical absorption.

INTRODUCTION

In the past decade, porous silicon (PS) has attracted considerable interest due to its potential application in the development of silicon-based optoelectronic devices [1,2]. However, the origin of the photoluminescence (PL) is still controversial, and numerous models proposed to illustrate the luminescence mechanism [1,3–18]. One type of model, such as quantum confinement model [1] and silicon intrinsic surface states model [3], considered luminescence to be an intrinsic effect of nanometer Si. Another type of model attributed the luminescence from PS to some special luminescent materials rather than an intrinsic property of nanometer Si [2–12]. A third type of model, called the quantum confinement/luminescence center (QCLC) model [13], claimed that photoexcitation of electron-hole pairs occurs in the nanometer silicon particles (NSPs), but most of the photoexcitated electrons and holes transfer from the NSPs into the luminescence centers (defects or impurities) in the surrounding SiO_x layers or at the interfaces between NSPs and SiO_x and radiatively recombine there.

Since the first work on comparing the optical transmission of bulk Si with that of free-standing PS films by Lehmann and Gösele [19], optical transmission measurement has become one of the most powerful tools for understanding the microstructure and luminescence mechanism of the PS. Lehmann and Gösele attributed the increasing of the transmission below the direct gap to quantum confinement effects [19]. Sagnes et al. [20] have measured the transmission of the free-standing p^+ and p^- PS films with porosities in a range of 45–79% and observed a continuous blue-shift of the transmission curves with and increase in the porosity of the PS films. Measurements of the spectra dependence of the absorption in the p^+ PS films showed that it follows the behavior expected for indirect semiconductors [20]. As to p^- PS, an exponential increase of the absorption coefficient with energy is observed, but the absorption behavior characterizing direct semiconductors has not been observed [20]. Kovalev et al.

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[21] have measured the temperature dependence of the absorption coefficient of PS and indicated that phonon-assisted optical absorption took place as expected from the indirect nature of crystalline silicon in contradiction to the prediction of the quantum confinement model and the Urbach tail-state model. Xie [22] observed that the blue-shift of the PL peak position coincided with that of the absorption spectra. Kanemitsu [14] reported that there was no clear size dependence of the PL peak energy, whereas an obvious blue-shift of optical absorption was observed with a decrease in the average diameter of Si crystallites. Behren et al. [23] demonstrated unambiguously and quantitatively the role of quantum confinement in the optical properties of PS with porosities up to 92%. Recently, we have compared the PL spectra with the absorption spectra of PS samples with porosities in a wide range [24–26]. A continuous blue-shift of the transmission curves of PS samples with increasing porosity from 41 to 94% were also observed, but there was no correlation between the PL with optical absorption spectra of PS [25].

However, the evolution of the optical transmission of the PS modified by oxygen is very surprising. Vincent et al. [27] observed a red-shift of the transmission curve under thermal oxidation at 400 °C for 1 h. We have reported that the transmission curve red-shifts and then blue-shifts during thermal oxidation process [26]. In this paper, we present a detailed study of the evolution of the optical absorption of the free-standing PS films under thermal oxidization at 200 °C in air. Further, the influence of the surface chemical species on the optical bandgap of the PS is discussed.

EXPERIMENTAL

The p^+ and p substrates used were (111)-oriented p-type silicon wafers, with resistivities of 0.01–0.015 and 2–4 Ωcm, respectively. Before the anodization, thin Al films were evaporated on the back of the wafers to form a good Ohmic contact. Free-standing PS films with porosities below 80% were formed by anodization in a HF-ethanol solution at constant current density. The current density (between 30 and 100 $mAcm^{-2}$) and HF concentration (between 20 and 35%) were adjusted in order to obtain the desired porosity. The PS films were then detached from the substrates by electropolishing at current density about 500 mA/cm^2. Free-standing PS films with porosities higher than 80% were prepared by the electrochemical etching-electropolishing, chemical dissolving, and supercritical drying method. A detailed description of the experimental procedure and apparatus are given in previous papers [24,25]. All of the free-standing PS films samples were oxidized in air at 200 °C for 40 or 200 h accumulatively.

The transmission spectra measurements were performed on an UV-vis-NIR recording spectrophotometer (UV-3100, Shimadzu) from 2000 to 400 nm. Raman spectra were obtained using 632.8-nm laser light from a He–Ne laser and a Raman microprobe measurement system (Micro Raman System 1000, Renishaw, England).

RESULTS AND DISCUSSION

The transmission spectra of the free-standing p PS films with porosities of 58, 68, 79, and 87% are shown in Fig. 1. The thicknesses of all of these PS films were about 40 mm. In this figure, we observed a continuous blue-shift of the transmission curves of PS samples with increasing porosity from 58 to 87%. Meanwhile, we also observed that the transmission at the low energy (the plateau region), T_0, increases with porosity. The blue-shifts of the transmission are correspondent to the results given elsewhere [20–25].

Figure 2 shows four Raman spectra of the free-standing p PS films with porosities of 58, 68, 79, and 87%. It is clearly shown that the Raman spectra were shifted to lower energy and broadened with increasing porosity of the PS. The solid lines in Fig. 2 are theoretical fitting for each experimental curve using the model for Raman line shape given in refs. 28 and 29. The average diameter (L) of the free-standing PS film with porosities of 58, 68, 79, and 87% are 3.4, 3.0, 2.6, and 2.3 nm, respectively.

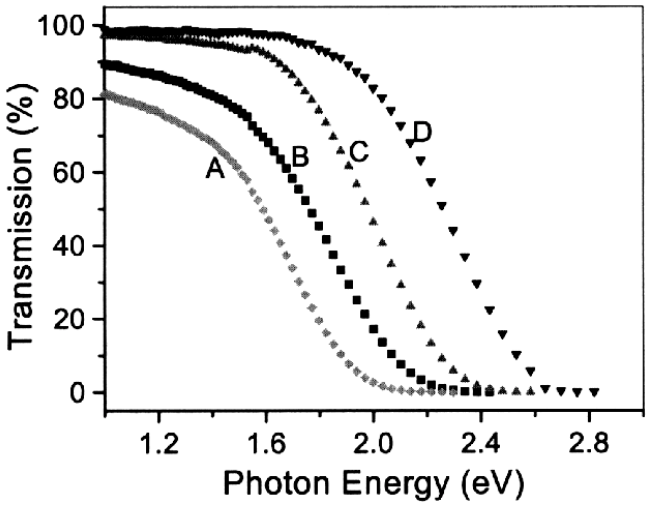

Fig. 1 Transmission coefficient vs. photo energy for free-standing porous silicon films with porosity of 58% (A), 72% (B), 81% (C), and 87% (E).

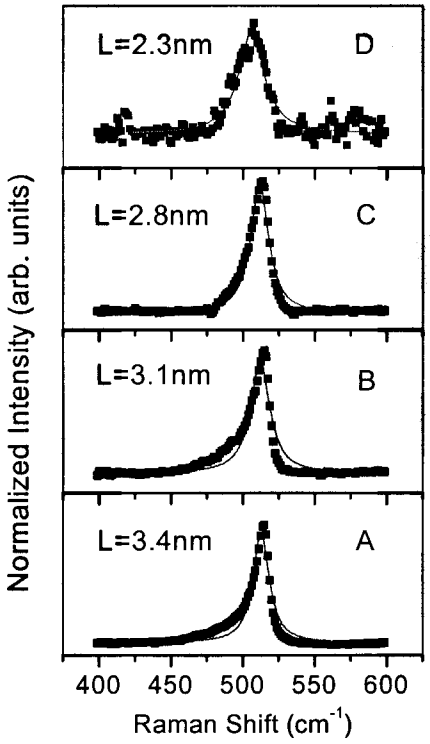

Fig. 2 Raman spectra of the free-standing porous silicon films (full squares) with porosities of 58% (A), 72% (B), 79% (C), and 87% (D). The dotted lines are the theoretical fitting to the experimental data.

The transmission spectra of p PS films with a porosity of 75% under thermal oxidized condition are shown in Fig. 3. After thermal oxidation for 40 h, the color of this film changes from red to brown and appears less transparent. In the meantime, a red-shift of the transmission curve and a decrease in the T_0 are observed. However, when we prolong the time of thermal oxidation to 200 h, the transmission curve obviously blue-shifts, and the T_0 increases.

Furthermore, we have compared the transmission curve of the as-prepared PS films with that of the oxidized and the deoxidized PS films. The transmission versus photon energy for the free-standing

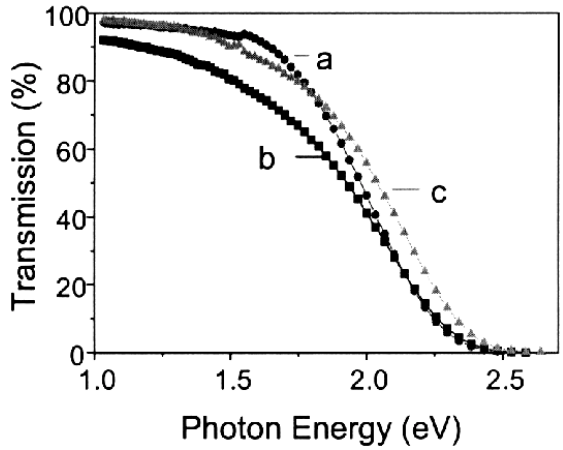

Fig. 3 Transmission coefficient vs. photon energy for a free-standing PS films with a porosity of 75%: (a) as-prepared, (b) oxidation for 40 h, and (c) oxidation for 200 h in air at 200 °C.

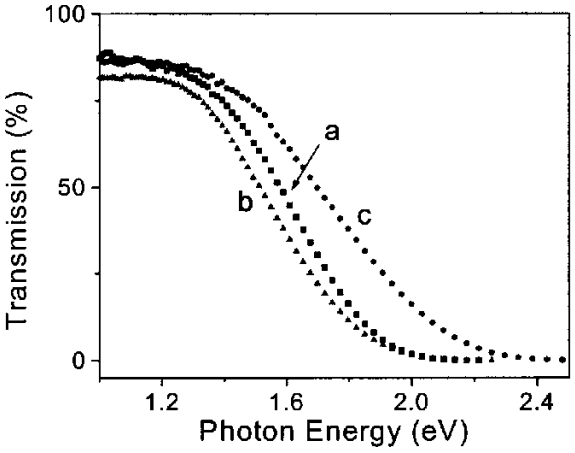

Fig. 4 Transmission coefficient vs. photon energy for a free-standing p^+ PS films with a porosity of 62%: (a) as-prepared, (b) thermal oxidation for 40 h, and (c) chemically deoxidized.

p^+ PS films with a porosity of 62% is shown in curve (a) in Fig. 4. After thermal oxidation at 200 °C for 40 h, the transmission curve is red-shifted (curve b), which is similar to the observation in Fig. 3. After removing the oxide layer in 40 wt% HF solution for 1 min, the porosity of the resulting films have increased from 62 to 74%, and the transmission curve (Fig. 4c) is obviously blue-shifted relative to curve (a).

Figure 5 shows three Raman spectra of free-standing PS films with porosities of 58 and 85% under oxidation at 200 °C for 0, 40, and 200 h. Downshift and broadening of the Raman spectra with prolonging the time of thermal oxidation are also observed in these films. Solid lines in Fig. 5 are fitting curves, which coincide with the experimental dates quite well. The average diameter (L) of the as-prepared samples with a porosity of 58% by fitting the Raman spectra is 3.4 nm. After thermal oxidation at 200 °C for 40 and 200 h, the average diameters decrease to 2.2 nm and 1.7 nm, respectively.

It is generally accepted that the blue-shift of the transmission curves with increasing porosity or decreasing the size of the NSPs is due to the quantum size effect. According to the quantum confinement effect, the energy gap associated with each crystallite should increase with the decrease in the size of the NSPs, and thus the transmission curve should be blue-shifted. Our experimental results in Figs. 1 and 2 confirm that the behaviors of the optical absorption of the fresh PS films can be explained by the

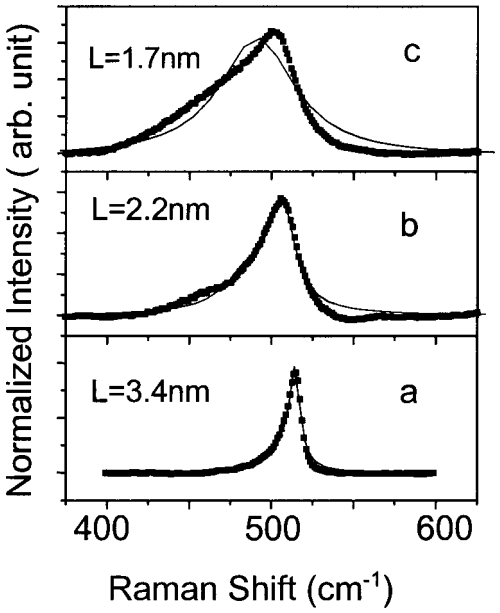

Fig. 5 Raman spectra of a free-standing p PS films with a porosity of 58%: (a) as-prepared, (b) oxidation for 40 h, and (c) oxidation for 200 h in air at 200 °C. The dotted lines are the theoretical fitting to the experimental data.

quantum confinement effect. However, the evolution of the transmission curve of the oxidized free-standing PS films is very surprising. Our experiment result, in Fig. 4, indicates that the transmission curve red-shifts and then blue-shifts during thermal oxidation. In the meantime, the transmission at the low energy decreases first and then increases. Why does the oxidized PS sample show this surprising and complicated behavior?

It is well known that the Si dangling bonds on the surface of the as-prepared PS have absorbed a large mount of H to form weak Si–H bonds, which are easy to be oxidized by oxygen in air. During the thermal oxidation process, the surface would immediately cover with O instead of H, and the oxidation extent of PS would increase with the prolonged time of oxidation [26]. Furthermore, the average sizes of NSPs in free-standing PS films would continuously decrease during thermal oxidation, which is confirmed by the Raman scattering spectra shown in Fig. 5. Obviously, the optical absorption properties of the oxidized free-standing PS films are not in agreement with the predication of the quantum size effect.

Vincent et al. [27] suggested that the red-shift of transmission curves may be explained by the formation of a hypothetical (Si, O, H) absorbing compound, which is less transparent than PS, instead of a pure oxide, or a change in the surface or near-surface state energy depending on H or O passivation. Kumar et al. [30] obtained theoretically a conclusion that an increase in oxygen termination atoms produces a decrease in the energy gap of the NSP units. The above suggestions can explain the red-shift of the transmission curves, but cannot explain our experiment result on the transmission curve, in which the transmission curve red-shifts and then blue-shifts.

We propose an explanation as follows: (1) The energy gap associated with each crystallite should increase during thermal oxidation process, due to the quantum confinement effect. This hypothesis is supported by our experimental results in Figs. 3 and 5. (2) The energy gap should decrease with an increase in oxygen termination atoms. Both the increasing of the gap due to the quantum confinement effect and the decreasing of the gap due to the Si–O bond formation cause a complicated evolution of optical absorption. During the early stage of thermal oxidation, a rapid increase of Si–O bonds may be the major factor to affect the energy gap, thus leading to a decrease of the energy gap and a red-shift of the transmission curve. After a long time of thermal oxidation, the decrease of the energy gap caused by

an increase of Si–O bonds is saturated. In addition, the size of NSPs is very small, and a little further decrease of the size would result in a large increase in the energy gap. So, the energy gap will increase, and the transmission curves will blue-shift.

CONCLUSION

In summary, we have investigated the evolution of optical absorption properties of free-standing PS films during thermal oxidation at 200 °C in air. For as-prepared PS films, a continuous blue-shift of the transmission curves of PS samples with increasing porosity from 58 to 87% was observed. Theoretically fitting for Raman scattering curves indicated that the sizes of NSPs in free-standing PS films continuously decrease with an increase in the porosity or a prolonging of the time of thermal oxidation. The transmission curve red-shifts first and then blue-shifts during thermal oxidation. At the same time, the transmission at the low energy decreases first and then increases. This abnormal result can be explained by a model including the quantum confinement effect in the NSPs and the influence of the Si–O bonds on the surface of NSPs.

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