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Surface Structures and Photoluminescence Mechanisms of Porous Si

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The position of the valence band maximum, the Si 2p core level and the Si *L* threshold of porous Si (PS) have been simultaneously measured using synchrotron radiation. The measured surface optical gap is strongly correlated to the photoluminescence (PL) peak energy. This result indicates that the surface band gap and the surface region are related to the PL origin. Change in the band gap of PS relative to that of crystal Si is divided into almost the same amount of shifts in the conduction band edge and in the valence band edge, suggesting that quantum size confinement is the reasonable candidate for the PL origin. As freshly prepared PS contains almost no oxygen, oxidation acts as secondary effects in the PL mechanisms.

1. Introduction

Since the discovery of the intense visible photoluminescence (PL) in porous Si (PS)[1,2], most of the research on PS has been directed at understanding the origin of the light emission. This photoluminescence initially attributed to the formation of Si microstructures in the PS layer[1] that gave rise to quantum confinement effects. As the Si microstructures, thin Si columns and Si fine crystallites has been so far reported[3,4]. A recent Raman study has suggested that the local structure of PS is more like a sphere than a rod, and that the structure does not consist of a series of parallel columns[5]. Si crystallites with a size of ~ 3.5 nm has been also observed by cross-sectional high-resolution transmission electron microscopy[6].

Other candidates for the PL origin include a amorphous Si structure, with Si-H bonding termination[7,8], or surface species such as Si-H_x[9] and siloxene[10]. From thermal annealing experiments, it is indicated that Si-H_x is strongly related to the PL mechanisms[9]. However, some researchers have recently reported no correlation between the PL and surface hydrogen species[11,12]. On the other hand, oxidation of a PS surface leads to a degradation[13] or an enhancement[14] of the PL intensity depending on the oxidation method. Thus, surface structures and species may be directly linked with the PL origin itself or may work as secondary effects. Therefore, characterization of PS surface structures and species is essential to distinguish the surface effects and the bulk effects in the PL mechanisms. However, this characterization is not easy, because oxygen atoms easily bond to the PS surface under usual atmospheric condition.

In this work, both the surface characterization and the PL measurement of PS samples have been performed under vacuum condition without exposing the samples to air after and during the sample formation. The PS surfaces have been characterized using a synchrotron radiation photoemission technique (SRPES). The results show that the surface band gap of PS well trace the value of the PL peak energy and both the conduction band minimum (CBM) and the valence band maximum (VBM) move toward the opposite direction by almost the same energy when the sample preparation conditions are changed. There is also no strong indication that oxygen relates to the PL origin. These results indicate that quantum size effects play a central role in the PL mechanisms and oxygen acts as secondary effects.

2. Experimental

PS samples were prepared by anodizing p-type 2~6 ohm-cm Si(100) wafers in a mixture of a 55 wt % aqueous HF solution and ethanol with the ratio of 1:1 at anodization current densities ranging from 10 to 200 mA / cm^2 for 30 s.

To investigate the role of PS surface oxidation in the PL mechanisms, light-exposed PS samples were prepared[15]. These PS samples were formed by anodizing at an anodization current density of 80 mA / cm^2 for 60 s, then, they were kept in the same solution under light exposure with a 500 W tungsten lamp for up tp 480 s. This light-exposure treatment causes the oxidation of the PS surface as described in the next section. In other words, this treatment was used for oxidation of PS surfaces.

SRPES measurements were carried out using 0.4 GeV electron storage ring at the Synchrotron Radiation Laboratory of the Institute for Solid State Physics, the University of Tokyo. Photoemitted electron energies were analyzed using a double-pass cylindrical mirror analyzer contained in a ultra-high vacuum chamber with a base pressure of $< 5 \times 10^{-11}$ Torr. With this photoemission system, valence band spectra, Si 2p core spectra, and total yield spectra were obtained. The energy resolutions were 0.43 eV for the valence and core spectra and 0.05 eV for the yield spectra.

Photoluminescence spectra of the PS samples were measured using a 325 nm light of a He-Cd laser in a vacuum chamber .

3. Results and Discussion

Valence band spectra obtained from porous

Si formed by anodization at current densities ranging from 10 to 200 mA / cm² for 30 s are shown in Fig. 1. PL is easily recognized by eye for the PS samples anodized at current densities above ~100 mA / cm². A PL intensity from the PS sample anodized at 200 mA / cm² is more than 20 times as strong as that from the PS sample anodized at 100 mA / cm². In Fig. 1, intensities of O 2s peaks at ~26 eV are varied among the valence band spectra. However, an O 2s peak for the sample anodized at 200 mA / cm², which exhibits the most intense PL, is fairly small. In the spectrum of this sample (curve (d)), four distinct peaks, labeled I, C, D, E, are observed at ~3.6, ~6.2, ~9.0, and ~10.8 eV, respectively. The peak I is attributed to the p-derived valence band states16) and the C-D-E structure[16] is attributed to the characteristic states induced by a Si-H monohydryde configuration on the sample surface. As is shown in the valence band

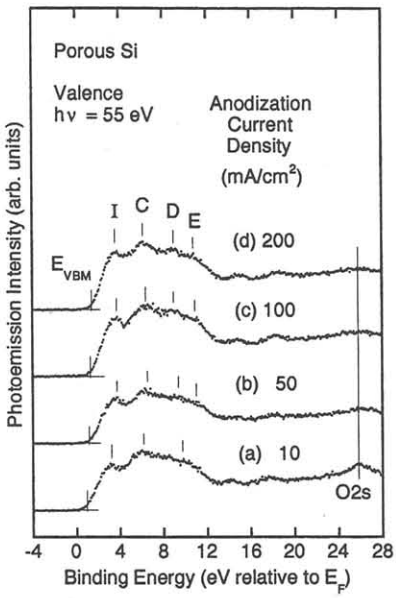

Fig.1 Valence band spectra obtained from porous Si formed by anodization in a HF solution at a current density of (a)10, (b)50, (c)100, (d)200 mA / cm² for 30 s.

spectra obtained from oxidized PS samples, an O 2p peak emerges between the peaks C and D. This O 2p feature does not observed in the curve (d), either. These result indicate that there is almost no trace of oxygen bonding on a PS surface, and exclude the siloxene and the oxide species as the PL origin.

Valence band spectra obtained from porous Si with the light exposure treatment are shown in Fig.2. As the light exposure time increased, the structures I and E become gradually obscured and the O 2p and O 2s peaks clearly emerge. The PL intensity is drastically enhanced when the light exposure time is 480 s. Therefor, the light exposure treatment, described in this research, causes the oxidation of a PS surface and an enhancement in the PL intensity. Considering the results in Fig.1, oxygen acts as secondary effects in the PL mechanisms.

Band gaps (Eg) and CBM and VBM energy positions (E_{CBM}, E_{VBM}) of the PS sample surfaces, with and without the light exposure treatment, were evaluated using the valence and core spectra and the total yield spectra. Figure 3 shows the example of the $L_{II,III}$ total yield spectrum obtained from the PS sample, which was formed by anodization at a current density of 10 mA / cm² for 30 s without the light exposure treatment.

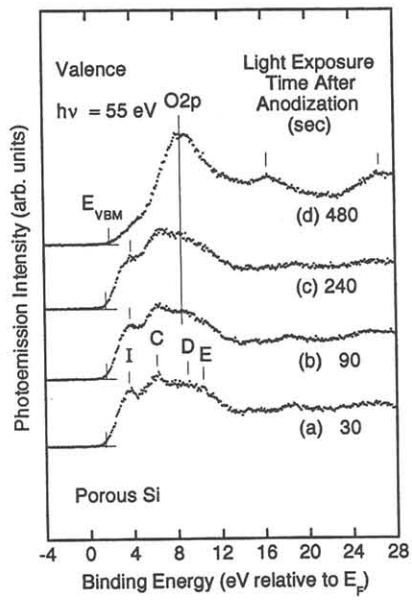

Fig.2 Valence band spectra obtained after light-irradiating porous Si, formed by anodization in a HF solution at a current density of 80 mA / cm² for 60 s, for (a)30, (b)90, (c)240, (d)480 s in the same solution using a 500 W tungsten lamp.

At around the middle of the rising slope in this total yield spectrum, an inflection point is observed. The appearance of this point is due to the Si $2p_{3/2}$-$2p_{1/2}$ spin-orbit splitting. The threshold (E_{th}) of the $L_{II,III}$ absorption, which corresponds to the transition to conduction states from $2p_{3/2,1/2}$ states, is determined to be the inflection point. The initial state of the transition corresponding to the inflection point is taken to be the peak energy position (E(Si $2p_{3/2,1/2}$)) in the Si $2p_{3/2,1/2}$ spectrum. Using the E_{VBM} value, the band gaps Eg is estimated by

$$Eg = E_{th} - (E(Si\ 2p_{3/2,1/2}) - E_{VBM}) + E_{XC} ,$$

where E_{XC} is the core exciton binding energy and the position of E_{VBM} is determined to be the leading edge of the valence band. From our own experiments, the E_{XC} value has been determined to be ~230 meV for crystal Si(100). This value is in good agreement with the previously reported values[17,18]. Using the Eg values and EVBM positions of the PS samples with respect to that of crystal Si, the E_{CBM} positions of the PS samples are also obtained with respect to that of crystal Si.

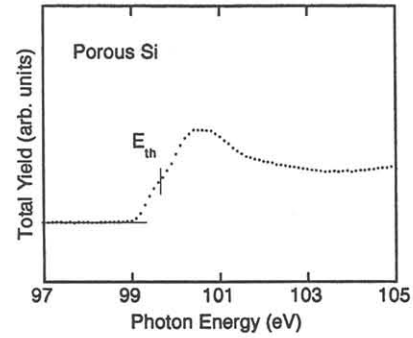

Fig.3 An example of a total yield spectrum. This spectrum is obtained from porous Si formed by anodization in a HF solution at a current density of 10 mA / cm² for 30 s.

The Eg values and the E_{VBM} and E_{CBM} positions of both a crystal Si surface and the PS sample surfaces, used in this work, have been estimated assuming that the E_{xc} value is constant, and these values are shown in Figs. 4 and 5. In these figures, the PL peak energy positions are also plotted. When the sample preparation conditions are changed, The surface band gap well traces a shift in the PL peak energy. This indicates the surface band gap and the surface structure are strongly related to the PL origin. Our fourier transform infrared spectroscopy (FTIR) experiments[19] also support the fact that the PL region is limited to the surface area of PS. Figure 4 also apparently indicates that the PS band gap is widened compared to the value of crystal Si, and that the light exposure treatment further widened the gap. As the anodization current or the light exposure time increases, the CBM position moves upward and the

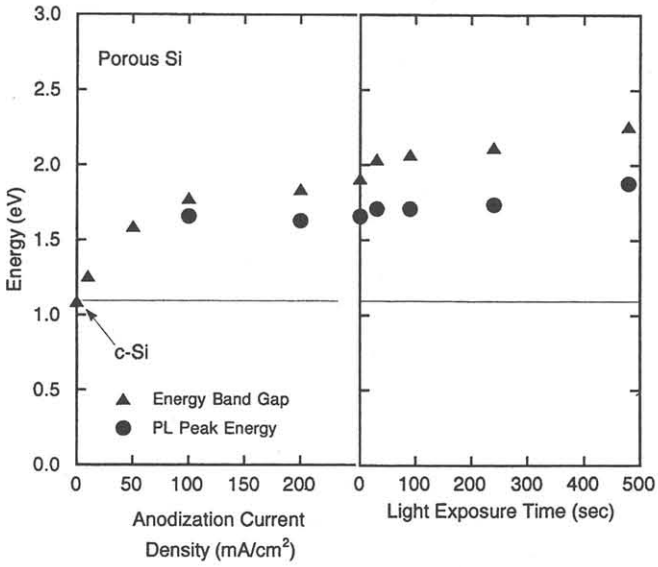

Fig.4 Energy band gaps and PL peak energies obtained for porous Si with (right part panel) and without (left part panel) a light-exposure treatment. The energy band gaps are evaluated using valence, Si 2p core and total yield spectra.

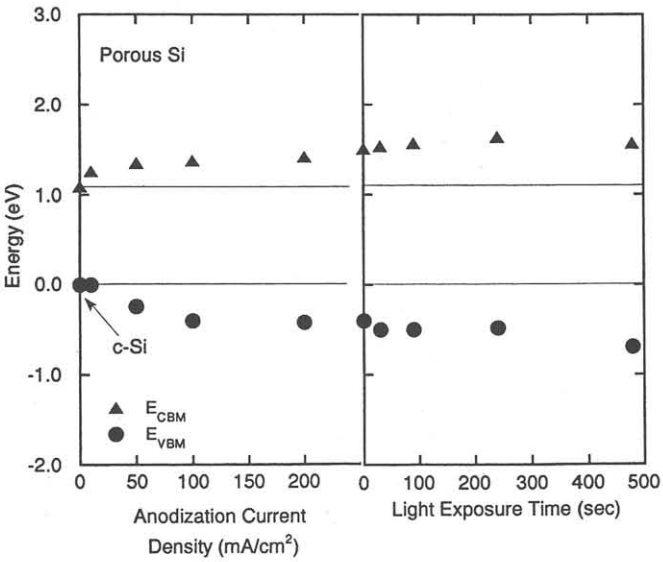

Fig.5 Energy positions of conduction band minimum (CBM) and valence band maximum (VBM) obtained for porous Si with (right part panel) and without (left part panel) a light-exposure treatment.

VBM position moves downward. This movement is contrary to the case of amorphous Si where the almost only VBM position is changed relative to that of crystal Si, indicating that band gap widening in PS is mainly due to quantum size confinement caused in the microcrystallite region formed on the surface area.

4. Conclusion

In conclusion, the surface optical gap of PS is strongly correlated to the PL peak energy, indicating the structures in the surface region are related to the PL origin. Change in the band gap of PS relative to that of crystal Si is divided into almost the same amount of shifts in the conduction band edge and in the valence band edge. The light irradiating PS in a anodization solution leads oxidation and a blue shift in the PL. As freshly prepared porous Si does not contain oxygen, oxidation acts as secondary effects in the PL mechanisms.

Acknowledgment

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