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Visible Photoluminescent Properties of Porous Silicon

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Optoelectronic properties of porous Si (PS) have been studied in terms of photoluminescence, photoconduction and optical absorption. The PS layers are formed on p- and n-type Si wafers by the electrochemical anodization. Macroscopic observations (efficient visible PL at room temperature, apparent photoresponse for visible light, a significant bandgap widening and retention of the crystallinity) suggest quantum size effects in PS.

1. Introduction

Porous Si (PS), formed by the anodic conversion of crystalline Si in dilute HF solutions, consists of a great number of micropores (2-50 nm in mean diam). Although the structural and material properties of PS have been characterized extensively, its photoelectronic properties are not known in detail. Recently, Canham[1] demonstrated visible photoluminescence (PL) from high-porosity Si at room temperature. We have studied the photoelectrochemical[2-5] and photoconductive[6] properties of PS, and suggested that its optical bandgap is present in the visible region. On the basis of that result, we reported in a previous paper[7] that as-anodized PS layers formed on p- and n-type nondegenerated Si wafers exhibit efficient visible PL emission. Here we report the somewhat more detailed PL characteristics of PS, together with some experimental data on its structural and optoelectronic properties.

2. Experimental

The PS layer was formed by anodization of single crystal Si wafers in 48wt% HF solutions using a Pt as a counterelectrode in the same way as that described previously.[7] Silicon wafers used in the experiments were nondegenerated p-type (8-20 Ω cm) and n-type (1-2 Ω cm) single crystals with a (111) mirror surface. The anodization current density was 10-80 mA/cm^2. For n-type Si substrates, anodization was carried out under illumination with a 500 W tungsten lamp from a distance of 20 cm in order to generate holes which are necessary for the dissolution of Si. The PS layers formed on p-type substrates are denoted hereafter by p-PS, while those on n-type substrates by n-PS. The PS thickness, controlled by anodization time, was 20-50 μm. The schematic illustration of the sample is given in Fig. 1. The PL spectra were measured by the conventional dc method[7] at room temperature. A 15 mW He-Cd laser (325 nm) or the filtered UV component of the light from a 500 W Xe lamp was employed for the excitation source. Besides PL, the photoconduction effect was investigated. For this measurement, a semitransparent thin Au film was deposited onto the PS layer surface. A 500 W Xe lamp was used as the light source. To evaluate the optical absorption of PS, self-supporting PS layers were prepared by separating the as-anodized PS layers from the Si substrates.

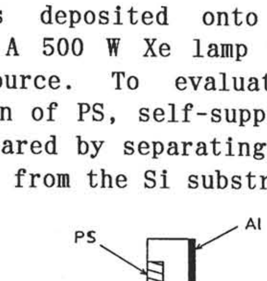

Fig. 1. Schematic illustration of the PS sample.

The separation of PS layers was performed by increasing the anodization current up to a level of electropolishing mode (about 400 mA/cm^2) immediately the PS growth was completed.

The structural analysis of PS itself was also carried out by X-ray diffraction measurements.

3. Results and Discussion

3.1 PL Characteristics of PS

Both the p-PS and n-PS layers showed an efficient visible PL at room temperature. As a typical example, the orange color PL spectrum for p-PS is shown in Fig. 2 by the solid curve. This sample was anodized at 25 mA/cm^2 for 15 min. In this measurement, UV light from a 500 W Xe lamp was used as the excitation source. The PL emission was very stable and reproducible.

The p-PS and n-PS layers also showed an apparent photoconduction effect for visible light, together with an extremely high resistivity in the dark. The spectral response of the photoconductivity of a p-PS layer is shown in Fig. 2 by the dashed curve. The anodization condition of this sample was the same as that of the solid curve. It can be seen that the peak wavelength of the photoconduction spectrum is about 500 nm. This implies that the topological modification of single-crystal Si produces a significant bandgap widening.

An efficient, stable and visible PL can be produced only by the introduction of a

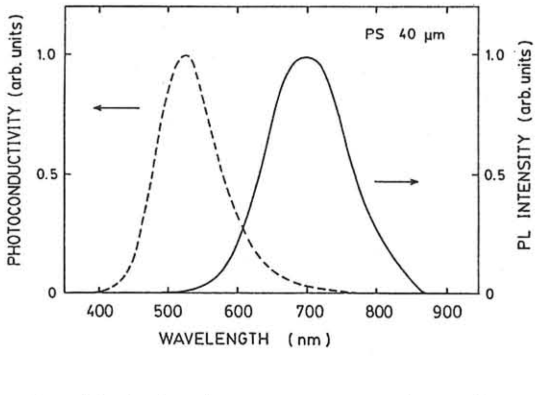

Fig. 2. Photoluminescence spectrum for a PS layer (40 μm thick). The resistivity of the Si substrate was 8-11 Ω cm. The corresponding photoconduction spectrum is also shown by the dashed curve. These two PS layers were anodized under the same condition.

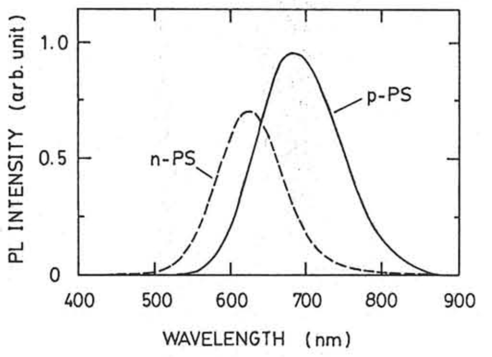

Fig. 3. PL spectra of p-PS (self-supporting, 40 μm thick, anodized at 10 mA/cm^2) and n-PS (30 μm, at 50 mA/cm^2).

porous structure into crystalline Si, despite its indirect band scheme. A possible explanation of this remarkable phenomenon is that some quantum size effects appear in thin Si column arrays. If this is the case, the peak wavelength of PL spectra should depend on the Si column width that is determined by the porosity of the PS layers. The porosity of PS can be controlled by the anodization parameters (the resistivity of the Si substrate, its conduction type, anodization current density and the anodizing HF concentration).

In fact, some correlation between the anodization variables and the PL spectra has been confirmed. Figure 3 shows two typical PL spectra of p-PS and n-PS at room temperature. In these PL measurements, the samples were excited with a He-Cd laser. The p-PS sample is a self-supporting PS film (40 μm thick). An apparent blue shift in the PL band can be observed for n-PS. In general, under similar anodizing conditions, the porosity of n-PS becomes large in comparison to that of p-PS. The result of Fig. 3 can, therefore, be regarded as a result of a particular type of size dependence on the electronic state in the quantized system, although the microscopic mechanism of PL emission has yet to be determined.

3.2 Related Physical Properties of PS

The fabrication of self-supporting PS layers has made it possible to describe quantitatively the physical properties of PS itself.

First, the optical absorption coefficient α of a self-supporting p-PS layer was determined from the optical transmission and reflection spectra measurements. The solid curve in Fig. 4 shows the α values versus wavelength for p-PS. In this figure, the data reported in the literature[8] for crystalline Si (c-Si) and hydrogenated amorphous Si (a-Si:H) are also shown. It is evident that the optical behavior of PS is distinctly different with that of c-Si and even of a-Si:H. The main edge of PS seems to be present in the visible region.

Second, the X-ray diffraction pattern for the same self-supporting p-PS layer as Fig. 4 is shown in the lower side of Fig. 5. The corresponding pattern for the original Si substrate is also shown in the upperside for reference. The PS layer certainly retains some of the original lattice order of the Si substrate, although there is a considerable lattice distortion and a consequent deterioration of the crystallinity.

The self-supporting PS exhibited an efficient PL as mentioned above. Visible PL emission comes from optical excitation of PS layer itself, so the result of Fig. 2 should not be related to some local phenomena at the PS-substrate interface.

These facts are consistent with the assumption that quantum size effects are induced in PS. To verify this explanation, however, more detailed analytical work needs to be done in relation to the electronic structure, electrical properties, optical response and interfacial photoelectronic properties. Particularly, the most important subject is to provide evidences that the PL emits from inside Si columns and that the optically excited substance leading to photoconductivity is Si crystallites.

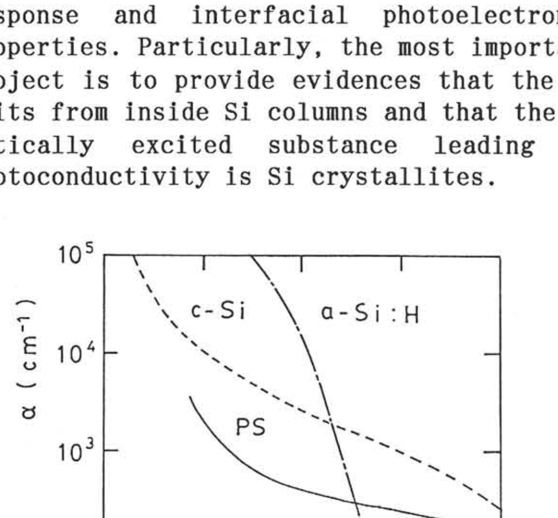

Fig. 4. Optical absorption coefficient versus wavelength for self-supporting p-PS.The PS layer (40 μm thick) was formed on p-type Si (10-20 Ω cm) at an anodization current of 10 mA/cm^2. Data[8] of crystalline Si and amorphous Si:H are also shown.

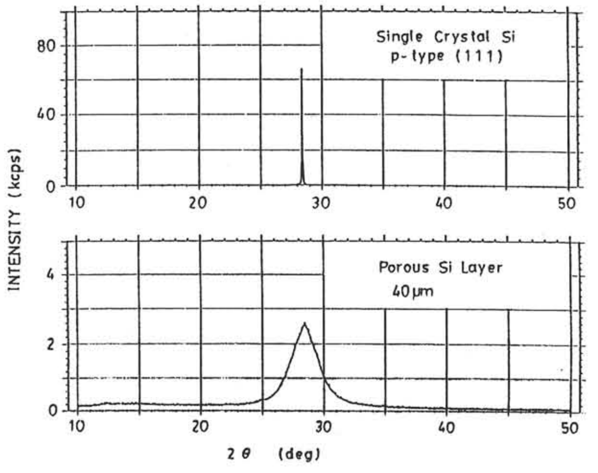

Fig. 5. X-ray diffraction patterns for p-PS and single-crystal Si. The PS layer is the same as that of Fig. 4.

4. Summary

As-anodized PS layers formed on p-type and n-type Si wafers exhibited an efficient visible PL at room temperature. Some information about the intrinsic nature of PS was obtained from the measurement of absorption coefficient spectra and X-ray diffraction analysis for self-supporting PS samples, which may support the quantum size effect model. There is a possibility that the visible luminescent property of PS breaks the band scheme constraints of single-crystal Si. More detailed studies concerning the electronic, optoelectronic and structural properties of PS are necessary in order to determine the microscopic mechanism of a visible PL emission.

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