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The effect of deuterium on the optical properties of free standing porous silicon layers

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Abstract. Free-standing porous silicon films with high deuterium concentration have been fabricated. Optical properties of the freshly produced samples have been studied using infrared spectroscopy and photoluminescence. A detailed analysis of photoluminescence and infrared absorption spectra was performed. Changes in the optical and photoluminescence properties, modification of the surface states of porous silicon layers during their exposure in the ambient air have been studied. The precise value of the vibration frequencies of the silicon-deuterium modes were obtained. The estimated value of refractive index of the porous silicon samples with deuterium is a factor of 1.6 higher than that of the samples with hydrogen.

Introduction

While there is strong evidence that light emission originates from Si crystallites, the difference of only 0.3 eV between the fundamental band gap E_g of Si and the red photoluminescence (PL) peak position, as well as the effect of chemical treatment on the PL spectra, indicates that the radiation process should be more complex than the simple confinement picture, and suggests, that the PL properties, the porous silicon (PS) microstructure and the surface chemical composition of the porous material should be correlated. The steady interest to these problems is justified from the point of view of their application of PS to electronic and optoelectronic devices.

Some researchers attempt to solve these problems by the variation of the current density, treatment time or electrolyte composition or by using electrolytes such as DF:C_2D_5OD [1] and HCl:HF:C_2H_5OH solutions [2] were made. They were able to verify that samples prepared by means of these electrolytes exhibit considerably better PL properties than samples obtained by means of the standard procedure.

Ipatova and co-worker [3] demonstrated that the quantity of deuterium (D) atoms in a sample of silicon must be greater than that of hydrogen atoms. Naturally that this result evoked great interest of the researchers which investigate problems of surface passivation of PS and its degradation.

Methods of the sample preparation and experimental techniques

Hydrogen terminated porous Si (H–PS, N1), and deuterium terminated porous Si (D–PS, N2) were formed by electrochemical anodizations. The H–PS was fabricated in the dark to avoid the oxidation using HF-ethanol solution (HF:H_2O:C_2H_5OH = 1:1:2) by applying

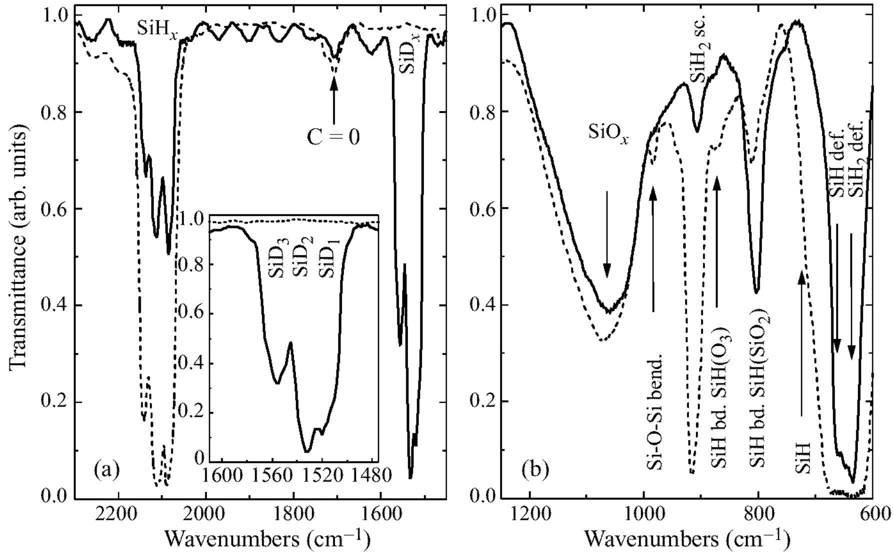

Fig. 1. Far-infrared vibrational spectra for the as-grown samples N1 (dotted curve) and N2 (solid curve). The insert shows the triplet structure of the Si–D$_x$ mode.

positive bias to a p-type 3–5 Ω cm Si substrate with a current density in the range of 15 A/cm^2 for 45 min. The D–PS were also fabricated in the same condition except for the use of DF-ethanol-D$_6$ solution (DF:D$_2$O:C$_2$D$_5$OD = 1:1:2) for 65 min. The free-standing porous Si layers were prepared by applying the electropolishing technique after the fabrication of the porous layer — we abruptly increased the current density up to 700 mA/cm^2 to remove the porous layer from the Si substrate.

The PL spectra were measured at sample temperature 300 K by using monochromator DFS-24. The PL was excited by a beam from Ar$^+$-ion laser ($\hbar\omega = 2.540$ and 2.409 eV, $P = 5$ mW in a spot of 3 mm^2 square). Absorbance and reflectance measurements were performed at room temperature in the wave number range from 20 to 5000 cm^{-1} using a Bruker IFS 113v Fourier transform infrared (FTIR) spectrometer. Instrumental resolution was 0.5 cm^{-1}. The spectrophotometer Hitachi 330 was used for registration of the absorption spectra. All spectra of the PS samples were measured two times: (1) as-grown; (2) after 6 months after they were stored in atmospheric ambient.

Experimental results and discussions

FTIR spectra

FTIR spectra of the samples N1 and N2 are shown in Fig. 1. The spectrum of the sample N2 shows a strong absorption in the range 1500–1570 cm^{-1}. On the contrary, this band is absent in a spectrum of the sample N1. The feature in this part of spectrum we can explain by the absorption of Si–D bonds in PS sample with deuterium. The fine structure of that absorption peak is demonstrated on the insertion of Fig. 1(a). It is important to note the next two factors. First, the structures of absorption bands SiH$_n$ and SiD$_n$ are similar. Second, isotopic shift of Si–D peak is 1.375. It coincides with the theoretical value of 1.376 [3]. In additionally, other well resolved another features have been observed in absorption spectra of the sample N1 and N2. The transmission spectra of the sample N1 and N2 in the range

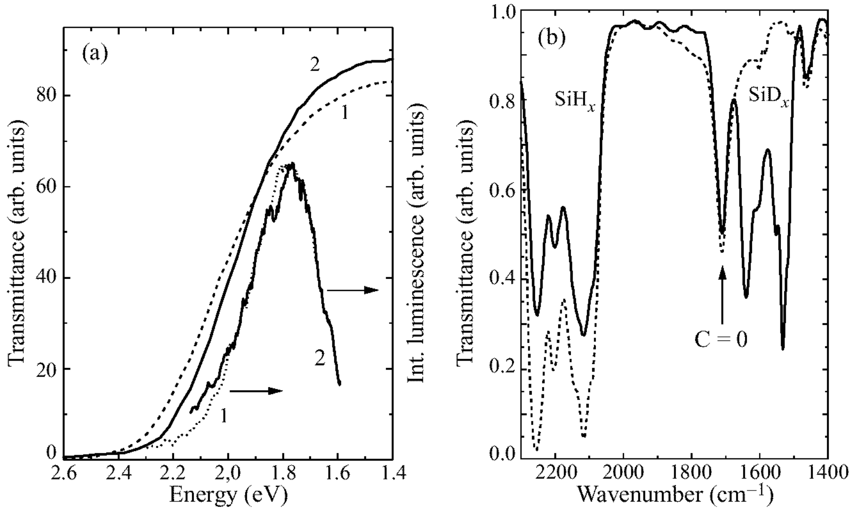

Fig. 2. (a) Optical-transmission and PL spectra of the as-grown sample N1 (dotted curve) and sample N2 (solid curve). (b) FTIR vibrational spectra of the samples after their degradation.

from 400 to 1300 cm^{-1} are demonstrated in Fig. 1(b).

Comparison of the hydrogen concentration which was estimated in the sample N1 and deuterium concentration in the sample N2 gives the ratio of $N_{D_2}/N_{H_2} = 1.06$. This ratio doesn't reach the value 5–6 obtained from [3]. However, the calculation obtained by Ipatova *et al.* [3] is valid for the equillibrium condition. Furthermore, the calculation which were carried out in [3] are related to the bulk semiconductors, but the diffusion of hydrogen and deuterium atoms on PS layer surface, especially during the process of nanocrystall surface formation, can be different from that in the case of the bulk monocrystall Si.

The transmission and reflection spectra of the sample N1 and N2 in the far-infrared (FIR) wavelength region (25–500 cm^{-1}) have the features connected with the light interference in a thin film of PS. It is possible to estimate the refractive index (n) of samples from these spectra knowing the thickness of the layer ($d_{\mathrm{N1}} = 50.0\,\mu$m and $d_{\mathrm{N1}} = 30.2\,\mu$m). We obtained $n = 1.52$ and 2.44 and from the transmission spectra $n = 1.60$ and 2.41 for the samples N1 and N2 correspondingly.

Photoluminescence and light absorption in the visible spectral rang

The absorption edge (E_g) of 1.81 and 1.83 eV for the sample N1 and N2, correspondingly was determined by the absorption measurements. Additionally, the photoluminescence spectra of these sample are shown in Fig. 2(a). The usual asymmetric form of the PL spectra with maximum at 1.769 eV (N1) and at 1.764 eV (N2) have been observed on the as-grown samples N1 and N2. The PL intensity of the fresh sample with hydrogen was similar to the sample with deuterium.

Degradation of the samples

The transmission spectra in the spectral region as in Fig. 1(b) of the sample N1 and N2 obtained after 6 months of exposure in the ambient air are shown in the Fig. 2(b). Careful analysis reveals essential peculiarities in the behaviour of the spectra. It is clearly seen the changes occurs at frequencies corresponding to the SiH$_n$ and SiD$_n$ stretching modes. From the change of the absorption ratio of the stretching modes (Si–D versus Si–H) before and after 6 months, we can show the effect of the gradual substitution from deuterium termination to hydrogen one as a function of aging time by comparing the results of Fig. 1(a) and Fig. 2(b). Also intensity of the absorption on the C = O (1720 cm^{-1}) bonds is increased. The spectral position of the PL peak of the sample with deuterium has not been changed. Very small change have been observed only in a high energy part of the spectrum. At the same time the PL peak of the sample N1 (with hydrogen) is shifted to lower energy ($\delta = 35$ meV). The dominant mechanism of radiative recombination in samples with hydrogen at the first moment after preparation is via excitons. The red shift upon oxidation is related to recombination involving a trapped electron or exciton [4].

It is known that the deuterium termination can significantly reduce the rate of the light-induced oxidation compared to hydrogen termination under the same oxidation condition [5].

Acknowledgments

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