Anisotropy of optical absorption in birefringent porous silicon

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Strong polarization-sensitive anisotropy of the optical absorption in the visible and infrared spectral range is observed in porous silicon (PSi) layers formed from bulk (110) Si wafers. It is shown that the anisotropy of the absorption via band-to-band and intraband (Drude-like) electronic transitions is consistent with the strong birefringence of these layers. Both phenomena are described by a model considering the form anisotropy in the (110) PSi layer assembled from nonspherical Si nanocrystals. We show that the anisotropic shape of the nanocrystals results in polarization-sensitive absorption by their surface silicon-hydrogen bonds. This allows an exact assignment of the stretching modes of silicon monohydride in the infrared absorption spectra of the PSi layers.

Crystalline silicon (c-Si) is an isotropic optical medium because it has a cubic lattice structure. It has been shown recently that nanostructuring of c-Si by porosification of low-symmetry Si surfaces[1,2] or by formation of micrometer-sized Si periodic structures[3] is appropriate technique to produce a strongly birefringent Si-based material. The reduced symmetry of the dielectric function of porous silicon (PSi) layers originates from the selective pore propagation in equivalent $\langle 100 \rangle$ crystallographic directions.[4] This preferential pore alignment has an important implication for the optical properties of the layers. In PSi layers formed from (110)-oriented c-Si wafers the projection of the pore propagation directions and remnant nanocrystal network on the (110) plane results in an uniaxial symmetry of the dielectric function being different for the $[1\bar{1}0]$ and $[001]$ in-plane directions. For the (110) PSi layers the birefringence (expressed in terms of the refractive indices difference) is very large, i.e., it reaches 0.3,[7] which exceeds significantly the values for natural birefringent crystals. Since the sizes of Si nanocrystals in microporous and mesoporous Si are much smaller than the wavelength of light, PSi can be considered as a homogeneous optical medium.[5,6]

The birefringence of PSi is shown[2,7,8] to originate from the form anisotropy[9] of Si nanocrystals and voids assembling the material. Microscopically, the phenomenon arises from the anisotropic depolarization fields screening the external electric field inside the nanocrystals and enhancing it in the voids. Since the probability of photon absorption in a single nanocrystal is proportional to the squared internal electric field the anisotropy of absorption is expected to be strong in birefringent PSi. In addition a strong anisotropy of absorption by the Si—H bond vibrations should occur because an anisotropic morphology of Si nanocrystals results in a preferential alignment of surface Si—H bonds present in as-prepared PSi layers.[10]

We report on the absorption anisotropy in birefringent (110) PSi layers in the visible and infrared spectral range. Three different absorption mechanisms have been investi-

gated: band gap absorption, free carrier absorption, and absorption by surface Si—H bonds. The importance of the local electric field for the absorption efficiency in an assembly of aligned nonspherical Si nanocrystals is demonstrated. Moreover, polarization-resolved IR absorption measurements allow to assign the Si—H stretching vibration modes.

PSi layers were prepared by electrochemical etching of single-crystalline (110) p-type ($\rho = 3$ mΩ cm) Si wafers in a HF:C_2H_5OH (1:1) solution at current densities $j = 25$–80 mA/cm^2 for 20–40 min. The free-standing PSi films were detached from the substrates by applying a short current pulse with $j = 500$ mA/cm^2. The porosity of the films measured by gravimetry was about 65–75 % depending on j. The thickness of the films determined from optical microscopy measurements was varied from 50 to 80 μm depending on the preparation conditions. Polarization-resolved optical absorption in the visible range was measured in transmission geometry by a single monochromator equipped with a charge coupled device. To investigate the IR optical properties of the layers a Bomem DA-3 FTIR spectrometer has been employed. Polarized IR measurements were carried out in the range from 1200 cm^{-1} to 5000 cm^{-1} with resolution of 2 cm^{-1} by using grating polarizers. The free standing PSi films were investigated in air (measurements in the vissible range) or in vacuum (FTIR experiments). All measurements have been performed at normal incidence and at room temperature. Reflection anisotropy has always been taken into account.

According to our transmission electron microscopy studies, typical sizes of Si nanocrystals assembling the PSi films exceed 10 nm.[7] Therefore, quantum confinement effects are negligible for the band gap of Si nanocrystals[13] (1.12 eV at room temperature[14]). Figure 1 shows the spectral dependence of the absorption coefficient of a (110) PSi film above the band gap of c-Si for two polarizations of light. The absorption coefficient for light polarized along the $[1\bar{1}0]$ in-plane direction ($\alpha_{[1\bar{1}0]}$) is larger than that for the perpendicular polarization ($\alpha_{[001]}$) over all spectral range investigated. The
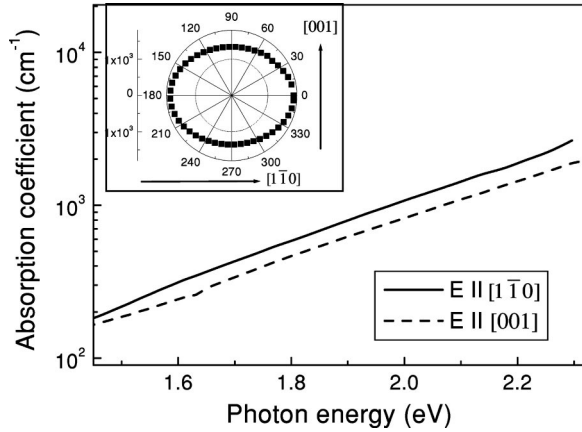
FIG. 1. Absorption spectra of a (110) PSi film measured for light polarization along the $[1\bar{1}0]$ (solid line) and $[001]$ (dashed line) in-plane directions. Inset: angular polarization dependence of the absorption coefficient at 2.17 eV.

ratio $\alpha_{[1\bar{1}0]}/\alpha_{[001]}$ is about 1.3–1.35 for photon energies 2.0–2.2 eV. The angular polarization dependence of the absorption coefficient (inset of Fig. 1) demonstrates an in-plane uniaxial symmetry of the layers. We note that a similar uniaxial symmetry has been observed for the refractive index of (110) PSi layers.[7,8]

From microscopic point of view the optical absorption anisotropy can be understood if the PSi layers are considered as an assembly of oriented nonspherical Si nanocrystals having larger dimensions along the $[1\bar{1}0]$ crystallographic axis. The external electric field of the optical wave induces polarization charges on the nanocrystal surfaces. The electric field inside the nanocrystals is smaller if the polarization vector of the external field is parallel to the smaller dimension of the nanocrystal. This results in a smaller probability of photon absorption in the PSi layers for light polarized along this direction. The screening efficiency is controlled by the dispersion of the dielectric function of c-Si. In fact, the $\alpha_{[1\bar{1}0]}/\alpha_{[001]}$ ratio increases slowly with photon energy (see Fig. 1) and the spectral dependence of the absorption coefficient corresponds to the normal dispersion of the dielectric function of c-Si.[14]

Figure 2 shows the spectral dependence of the absorption coefficient of a PSi film measured in the IR range for two directions of light polarization. A continuous absorption band due to absorption by free holes inherent for heavily boron-doped PSi is observed.[15] The sharp absorption peaks in the range of 2000–2200 cm^{-1} are due to the absorption by Si—H bond vibrations and will be discussed later. For frequencies below 1800 cm^{-1} the free carrier absorption follows approximately a power law with an exponent 2 typical for the classical Drude mechanism.[5] Again the absorption coefficient for light polarized along the $[1\bar{1}0]$ in-plane direction is always larger. This observation is in qualitative agreement with the results obtained for the visible range (see Fig. 1). The anisotropy of the Drude absorption depends on the birefringence which can be controlled by using different etching current densities for the PSi formation.[8] The value of birefringence can be easily calculated from the Fabry-Perot
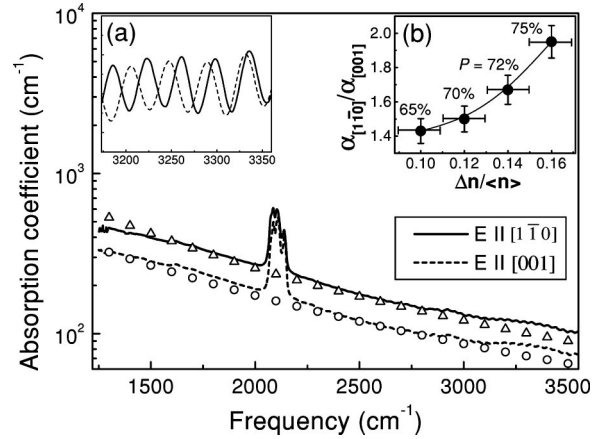

FIG. 2. IR absorption spectra of a (110) PSi film ($j = 40$ mA/cm^2, $P = 70\%$) measured for light polarization along the $[1\bar{1}0]$ (solid line) and $[001]$ (dashed line) in-plane directions. The corresponding absorption coefficients calculated by using formulas (1)–(3) are plotted by open triangles and circles. Inset (a) first derivatives of the transmittance of the film for two orthogonal light polarizations. Inset (b) anisotropy of the absorption coefficient vs the birefringence value normalized on mean refractive indices for the films prepared at $j = 25$, 40, 50, and 80 mA/cm^2 (porosity is marked at the corresponding experimental points).

interference fringes, which appear in the IR transmittance spectra in the range of small absorption. An example of the first derivatives of the polarized transmittance spectra is shown in inset (a) of Fig. 2. Based on these data, one can calculate both the birefringence $\Delta n = n_{[1\bar{1}0]} - n_{[001]}$ and the mean refractive index $\langle n \rangle = \frac{1}{2}(n_{[1\bar{1}0]} + n_{[001]})$, where $n_{[1\bar{1}0]}$ and $n_{[001]}$ are the refractive indices for light polarized along the $[1\bar{1}0]$ and $[001]$ in-plane directions, respectively. The values of Δn ($\langle n \rangle$) determined with accuracy of 10–15 % account 0.15 (1.63), 0.17 (1.50), 0.20 (1.48), and 0.22 (1.43) for the films prepared at $j = 25$, 40, 50, and 80 mA/cm^2, respectively. Inset (b) of Fig. 2 shows the ratio of $\alpha_{[1\bar{1}0]}/\alpha_{[001]}$ versus the ratio of $\Delta n/\langle n \rangle$. There is certainly a correlation between these values.

In order to describe both the absorption anisotropy and the birefringence we employ a generalization of the Brugger-man model.[17] This approach takes into account the morphological anisotropy of the PSi layers by modeling them as assembled from ellipsoids having parallel axes. The effective dielectric function ε_{eff} of PSi is then given by[18]

$$P\frac{\varepsilon_1 - \varepsilon_{eff}}{\varepsilon_{eff} + L(\varepsilon_1 - \varepsilon_{eff})} + (1-P)\frac{\varepsilon_2 - \varepsilon_{eff}}{\varepsilon_{eff} + L(\varepsilon_2 - \varepsilon_{eff})} = 0, \tag{1}$$

where P denotes the porosity and ε_1, ε_2 are the dielectric functions of the pores and nanocrystals, respectively; L is the depolarization factor dependent on the direction of the electric field with respect to the axes of the ellipsoids.

To model an optically negative crystal with the optical axis along the $[001]$ crystallographic direction lying in the (110) surface plane[2,8] of PSi one has to consider oblate ellipsoids of revolution (oblate spheroids) having larger axes a

and b ($a=b$) and a smaller axis c along the $[1\bar{1}0]$ and $[001]$ directions, respectively. The depolarization factor for the smaller axis of the spheroid L_c depends on the ratio between the axes lengths as[19]

$$L_c = \frac{x^2}{x^2-1}\left[1 - \frac{\arcsin[x^{-1}\sqrt{x^2-1}]}{\sqrt{x^2-1}}\right], \qquad (2)$$

where $x=a/c$. The depolarization factors for the larger axes are obviously $L_a=L_b=(1-L_c)/2$.

The dielectric function ε_2 in the IR range should include the contributions from the dielectric background and the free carrier susceptibility[5]

$$\varepsilon_2 = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\tau}, \qquad (3)$$

where $\varepsilon_\infty = 11.7$ is the high-frequency dielectric constant of c-Si, ω is the frequency of the IR light, τ is the scattering time of free holes and ω_p is the plasma frequency ($\omega_p^2 = 4\pi N_p e^2/m_p$, where N_p and m_p are the concentration and effective mass of free holes).

We found that both the birefringence and the absorption anisotropy are well described by the same effective medium model assuming the ratio of a/c ranging from 1.4 to 1.7 depending on P. The absorption coefficients calculated according to formula's (1)–(3) give $\alpha_{[1\bar{1}0]}/\alpha_{[001]}$ ratios in the range 1.5–2.1, which are in good agreement with the experimental results [see inset (b) of Fig. 2]. Figure 2 shows the calculated polarization-dependent absorption coefficient for an assemble of oblate Si spheroids placed in vacuum ($\varepsilon_1 = 1$, $P=0.68$). We used $x=1.4$ ($L_c=0.426$) to fit both the measured birefringence ($\Delta n/\langle n\rangle = 0.12 \pm 0.01$) and IR absorption curves for the film prepared at $j=40$ mA/cm^2. From the absolute strength of absorption we obtained the free hole concentration to be $N_p=1.3\times10^{19}$ cm^{-3}, which corresponds to $\omega_p=1800$ cm^{-1} ($m_p=0.2$). The best fit can be achieved assuming $\tau^{-1}=900$ cm^{-1} and 1250 cm^{-1} for the polarization perpendicular and along the c axis.[20] The ratio between the reciprocal scattering times along and perpendicular to the c axis is almost equal to the axes ratio x. Indeed the scattering for carriers moving in the direction of the smaller axis should be more efficient due to stronger surface scattering. This is why the measured absorption anisotropy is slightly larger for the intraband absorption region (compare Figs. 1 and 2). We note, that the absolute values of the refractive indices of birefringent PSi are also well described by the generalized Bruggerman model. These results will be published elsewhere.

Now we turn to the discussion of the anisotropy of the IR absorption by atomic bonds on the Si nanocrystal surface. Figure 3 shows silicon-hydrogen stretching vibration spectra where a featureless Drude absorption background has been subtracted for clarity. For as-prepared PSi films three well-defined peaks located at 2088, 2110, and 2137 cm^{-1} are resolved. Additionally there is a fine structure of the absorption bands consisting from at least six spectrally overlapping absorption lines. The absorption of IR light polarized parallel to
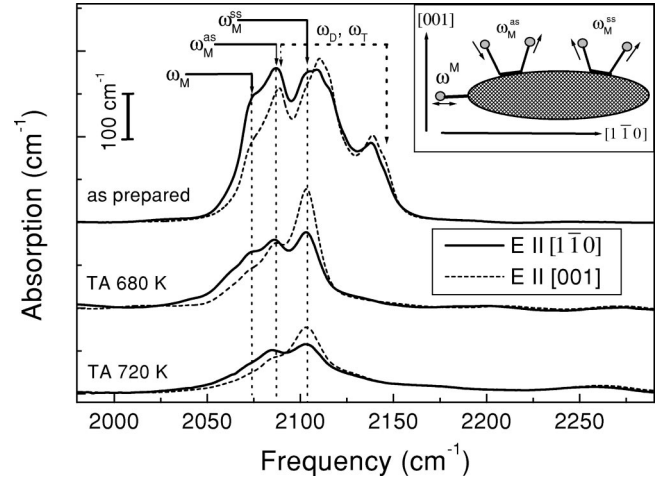

FIG. 3. IR absorption spectra in the spectral range of Si—H$_x$ stretching modes for as-prepared and annealed (110) PSi films measured for light polarization along the $[1\bar{1}0]$ (solid line) and $[001]$ (dashed line) in-plane directions. Monohydride bands (ω_M, ω_M^{as}, ω_M^{ss}) are indicated by arrows and vertical dotted lines. The region of the dihydride (ω_D) and trihydride (ω_T) bands is also indicated. Inset: sketch of the orientation and shape of a Si nanocrystal and the geometry of the in-plane monohydride vibrations.

the $[1\bar{1}0]$ direction is stronger in the range of 2050–2100 cm^{-1} while for the lines located at 2110 cm^{-1} and 2137 cm^{-1} it is stronger for the orthogonal polarization.

The experimental results for the as-prepared samples evidence the polarization anisotropy of the surface bond absorption bands but their assignment requires additional experiments. We performed the same FTIR studies for the samples thermally annealed in ultrahigh vacuum for selective hydrogen effusion. Annealing at $T\geq680$ K for 10 min leads to a disappearance of the absorption lines at frequencies above 2110 cm^{-1} and enhances the anisotropy of the surface band absorption, while the birefringence does not significantly change after this treatment.[21] Note, that the total integral of the absorption decreases more than twice after annealing. Our nonpolarized FTIR measurements in the range of the Si—H$_2$ scissors mode (912 cm^{-1}) demonstrate a complete desorption of the dihydride species for the treatment at $T\geq680$ K, which is in good agreement with Ref. 16.

The IR absorption spectra of thermally treated PSi evidence that the remnant lines between 2075 and 2103 cm^{-1} are the monohydride modes. They can be identified due to the morphological anisotropy of Si nanocrystals. Indeed, the surfaces of Si nanocrystals flattened in the $[001]$ direction should be covered with preferentially oriented Si—H bonds. Flattened surfaces of the spheroid shown in inset of Fig. 3 should be mainly covered by silicon-monohydride dimer H—Si—Si—H species. The relative concentration of monohydride dimers significantly increases after thermal annealing since this treatment produces Si dangling bonds which are required for the dimer formation.[22] Antisymmetric and symmetric vibrations of the monohydride dimers (see inset of Fig. 3) are favorably excited by light polarized along the $[1\bar{1}0]$ and $[001]$ directions, respectively. We attribute the

absorption line at $\omega_M^{as} = 2088$ cm^{-1} to the antisymmetric and at $\omega_M^{ss} = 2103$ cm^{-1} to the symmetric stretching vibrations of the monohydride dimers.

The surface termination by the monohydrides Si—H (one H atom vibrating against a Si atom backbonded to three Si atoms) is expected to be favorable for strongly curved surfaces of the spheroid. The electric field parallel to the $[1\bar{1}0]$ direction will excite vibrations of these bonds more efficiently. This conjecture is supported by data presented in Fig. 3 and therefore the line at $\omega_M = 2075$ cm^{-1} is due to the monohydride stretching vibrations. We note, that this assignment agrees with the results for an hydrogenated flat c-Si surface.[12]

To conclude, we have shown that the anisotropy of the optical absorption in (110) PSi layers is consistent with the anisotropy of their refractive index. Both phenomena originate from the form anisotropy of Si nanocrystals in the PSi layers. Polarization resolved IR absorption measurements on (110) PSi layers allow the assignment of silicon monohydride stretching modes.

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