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Birefringent nanostructured silicon: new promising material for linear and nonlinear optics

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Abstract. Porous Si layers produced by anisotropic electrochemical etching of bulk Si exhibit strong in-plane birefringence which depends on the sizes of Si nanocrystals, spacing between them and dielectric properties of their surrounding media. Second harmonic generation experiments have revealed phase matching conditions for wave interaction in the layers. Furthermore, they can serve as a phase-matching matrix for optically nonlinear substance incorporated in their pores. This finding can significantly expand the choice of nonlinear optical media since their anomalous dispersion is not strictly required for phase matching conditions.

Introduction

Crystalline silicon has indirect band gap and highly isotropic cubic lattice structure what limits its optical applications. Most of research efforts to eliminate its properties were devoted to porous modification of Si (PSi) produced by its electrochemical etching [1, 2]. The absence of a large volume fraction of Si results in a reduced value of the refractive index (n) of PSi. PSi prepared on (100) Si substrates is demonstrated to be in-plane optically isotropic due to the equivalence of [010] and [001]crystallographic directions [2].

To achieve in-plane uniaxial dielectric anisotropy we have employed the electrochemical etching of (110) Si wafers. Because of the selective crystallographic pore propagation in equivalent [010] and [100] directions tilted to the (110) surface [3] the projection of those on the (110) plane ([1$\bar{1}$0] direction) would result in an uniaxial surface symmetry with a dielectric constant $\varepsilon_{[1\bar{1}0]}$ being different from $\varepsilon_{[001]}$. Bulk Si is not anisotropic crystal but its porous modification becomes intrinsically uniaxial for this plane due to anisotropic dielectric nanostructuring. Since nanocrystals retain the diamond-like crystalline structure and their sizes (1–50 nm, depending on wafer doping and etching parameters used) [4] are much smaller than the wavelength of light, PSi still can be considered as a continuous optical medium. Therefore the effective medium approximation[5] can be applied to analyze the optical properties of PSi.

1. Experimental

PSi layers were prepared from (110) oriented, boron doped Si substrates with typical resistivity of 0.001–4 $\Omega\cdot$cm. The electrochemical etching was done in ethanoic hydrofluoric solution. The porosities of the layers were in the range from 50 to 70%. Free-standing PSi films were investigated by Fourier transform infrared (FTIR) spectroscopy. Optical transmittance of linearly polarized light was also measured to evaluate birefringence values in visible and near IR spectral regions.

The experimental set-up for second harmonic generation (SHG) consists of a picosecond Nd:YAG master oscillator with passive mode locking and amplification cascades. The second-harmonic signal was detected with a photomultiplier. The $\lambda/2$ plate was used to rotate polarization of fundamental wave. For details see [6].

2. Results and discussions

The clear evidence of the birefringence in anisotropically etched PSi layers comes from FTIR spectra measured for unpolarized light. Inset in Fig. 1 shows a typical reflectance spectrum at normal incidence. The spectrum exhibits interference fringes modulated by beats. The beats arise from the existence of two principal in-plane directions with different refractive indices and their difference (the birefringence) Δn is estimated to be about 0.18 while the mean refractive index n_m is 1.65 in the spectral range of 2–20 μm. We found that the birefringence level of PSi is mostly sensitive to the doping level of Si substrate and dielectric surrounding of Si nanocrystals. Figure 1 gives the values of Δn for three sets of the samples prepared on Si substrates having different doping levels and, therefore, different mean sizes of Si nanostructures (measured by TEM). Solid lines in Fig. 1 are fits according to the effective media approximation [5] for anisotropically spaced Si nanocrystals. A good agreement between the measurements and calculations shows that an increase of Δn for short wavelength arises mainly from the dielectric function dispersion of bulk Si.

The large birefringence of anisotropically etched PSi allows us to reach the phase matching conditions for nonlinear optical wave interaction. We consider both types of SHG in negative crystal (*ooe* and *oee*) with synchronism conditions $n_{1o} = n_{2e}$ and $(n_{1o} + n_{1e})/2 = n_{2e}$, correspondingly. For normal incidence of the fundamental radiation at 1.06 μm phase mismatch is less for the second type of interaction (*oee*). For the first-type synchronism the angle is of 54% with the optical axis. However, in this case the angle inside the material between the normal and synchronism direction is 36°, what is higher than the angle of the internal reflection. Thus, in air synchronism is not achieved in PSi film

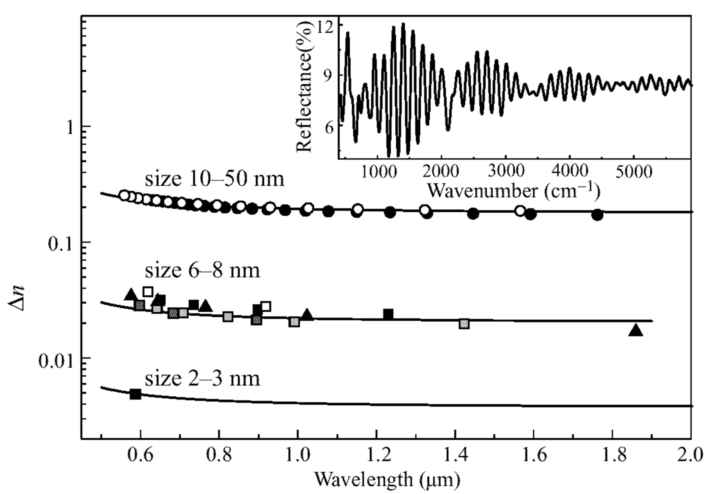

Fig. 1. Spectral dependence of the birefringence of PSi prepared on the substrates of p-Si (2–3 nm size of nanostructures), p^+-Si (6–8 nm size of nanostructures) and p^{++}-Si (10–50 nm size of nanostructures). Solid lines are fits according to the effective medium approximation. Inset: an example of the FTIR reflectance spectrum of PSi prepared on p^{++}-Si substrate.

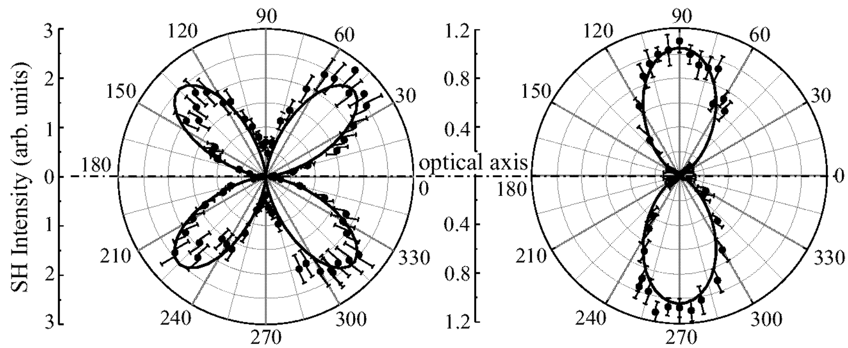

Fig. 2. Polarization dependences of the SH in PSi prepared on the p^{++}-Si substrate. The SHG experiments are performed in air at normal incidence of the fundamental radiation (a) and for incidence at 60° (b). Solid lines are theoretical fits.

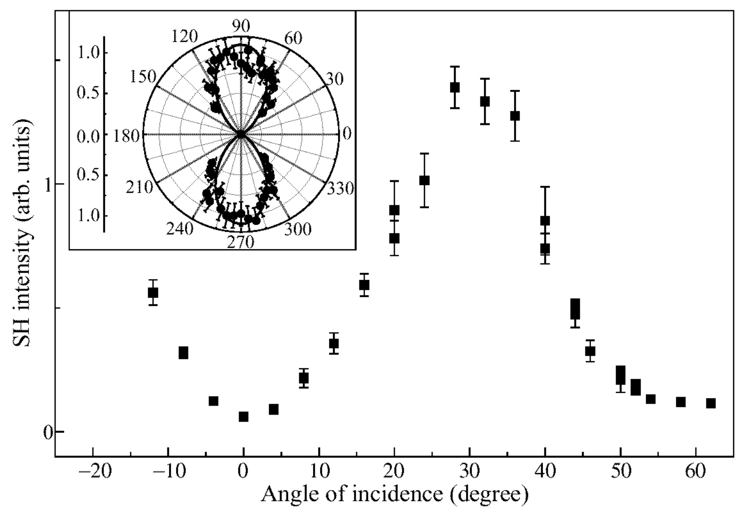

Fig. 3. Dependence of the SH in PSi (20 μm thick) on the angle of incidence. The pores of PSi are filled with glycerol. Inset: polarization dependence of the SH for normal incidence.

because its birefringence is too strong. The situation is changed when pores are filled with a dielectric media having a certain dielectric constant what reduces optical anisotropy. For example, according the effective media approximation the filling of the layer with glycerol ($n_g = 1.45$) gives the phase matching for *ooe* interaction at the angle of incidence of 31°.

Figure 2 shows dependences of the SH intensity for PSi on polarization of the pumping radiation. The SH is polarized along the optical axis of the PSi layer. If the pumping radiation falls normally to the surface the polarization dependence is two-fold (*oee* interaction), whereas for incidence at 60° it is one-fold (*ooe* interaction). The SH in the PSi layers filled with glycerol exhibits one-fold polarization dependence (inset in Fig. 3) independently on the angle of incidence. In fact, the filling of the pores with glycerol decreases anisotropy and, as a result, makes *ooe* interaction more effective even at normal incidence. The SHG in the layer filled with glycerol reaches the maximum for incidence at 30° (Fig. 3) what is in excellent agreement with our calculation for the phase matching condition. SHG in PSi is likely to be caused by bulk quadrupole nonlinearity because the elementary cells of

Si nanocrystals are rather centrosymmetrical [7]. The birefringence of PSi does not result in occurrence of effective dipole second-order susceptibility. The fact that maximal SHG efficiency in PSi with glycerol is observed at the expected angle of synchronism indicates that the phase matching can be achieved. This seems to be very promising for nonlinear optical applications since porous Si layers can play a role of a phase matching matrix for nonlinear media incorporated into its pores.

Acknowledgements

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