Light - Stimulated Anisotropy in Porous Silicon

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We report on the study of the polarization properties of the n-type microporous silicon. We have discovered the enhancement of the polarization memory effect when etching is carried out under illumination with linearly polarized light. Moreover, well-defined orientation dependence of the photoluminescence polarization level in the sample plane related to the polarization of the light used under anodization procedure have been found. We discuss this observation in terms of a preferential texture of the porous silicon layer induced by linearly polarized light-assisted etching.

I. Introduction

The correlation between polarization of excited light and polarization property of photoluminescence of the solids is well known. The study of the polarization properties of the light emission allows to identify the nature of the electronic transitions involved. There are several physical mechanisms responsible for these phenomena. However, the linear polarization memory effect of porous silicon photoluminescence^[1] cannot be attributed to the hot carrier alignment^[2], selective valley excitation in the multivalley semiconductors^[3] or anisotropy of absorption known for the $A^{II}B^{IV}$ nanocrystallites^[4]. This effect in porous silicon has been described in terms of anisotropy of optical properties of quasionedimensional silicon microcrystals that are responsible for the efficient porous silicon photoluminescence. The random distribution of the microcrystallites shapes and orientations leads to the absence of the anisotropy of the photoluminescence polarization level in the ordinary porous layer plane on the p-type Si (100) substrate^[1].

In this paper we report on the discovery of the enhancement of the polarization memory effect in n-type porous silicon when etching is carried out under illumination with linearly polarized light. We show that the etching conditions lead to the well-defined orientation dependence of the photoluminescence polarization level in the porous layer plane related to the polarization of the illuminated light.

II. Experimental

Anodization of n-type (100) Si substrate with resistivity 2-4 Ω cm is done in 50% HF etanoic solution (1:1 in vol.) during 20 min. at the current density of 20 mA/cm² The surface of the wafer is illuminated from Xe-lamp with the intensity of 0.1-0.2 W/cm². The light is linearly polarized along [110] or [100] crystalline silicon axis by a glass polarizer. The set of lowpass spectral filters is used to provide the defined spectral distribution of the incident light.

The photoluminescence is excited using 442 nm depolarized radiation from a He-Cd laser that is polarized by a film polarizer. Exciting light is normal to the surface of the sample. The polarization direction of the excited light is tuned by rotation of the polarizer. The photoluminescence is detected within the small angle aperture in the "backscattering" geometry. For the polarization degree measurements the second polarizer is placed between lenses of condensor and depolarizer in front of the entrance slit of the monochromator. The time-resolved luminescence measurements are done with the pulsed N_2 -laser ($E_{ex} = 3.67 \text{ eV}$, 10 ns pulse duration) and usual boxcar technique. The position of the 4 ns duration time gate is tuned in respect to the laser pulse with 1 ns accuracy. All spectra are normalized for the spectral response of the optical setup and measured at 300 K.

III. Results and discussion

The degree of the linear polarization ρ is determined as $\rho = I_{\parallel} - I_{\perp}/I_{\parallel} + I_{\perp}$, here I_{\parallel} is the intensity of the photoluminescence polarized parallel to that of the excited light and I_{\perp} is the photoluminescence intensity polarized in the perpendicular direction. The rotation of polarizers in the excitation and detection planes is done to measure the dependence of ρ versus polarization direction of excited light in the surface plane. Fig. 1 shows the photoluminescence and polarization degree spectra of two typical porous silicon samples prepared with linearly and randomly polarized illumination during anodization process. Photoluminescence spectra are linearly polarized throughout the all spectral range. However the enhancement of ρ can be easily seen for the sample prepared with linearly polarized light. We would like to point out the identity of the photoluminescence spectra.



Figure 1. PL and polarization degree (ρ) spectra of porous Si prepared with polarized (solid line) and unpolarized light (broken line).

The enhancement of ρ is much more pronounced on the blue edge of photoluminescence spectra (Fig. 1) and in this spectral region one should expect the influence of the fast blue luminescence band in the measured photoluminescence intensity and polarization level^[1]. Because of a huge difference in the lifetimes of the blue band (ns response) and red one (~ 10µs) it is very easy to extract the quantitative contributions from both of them in the time-delayed type of measurements. Fig. 2 shows the time-resolved photoluminescence and ρ spectra for two kinds of samples. These spectra are measured at the time gate position coinciding with the maximum of the laser pulse. Photoluminescence spectra exhibit the contribution of two luminescence bands, red with maximum at 2.0-2.1 eV and the blue one with the peak position at 2.7-2.8 eV. It is could be seen that the contribution of the blue band is negligible in respect of that of the red band. With increase of the delay time above 40 ns the blue band is disappeared. The amplitude of the red band is means that we could completely neglect the contribution of the blue band in the cw photoluminescence spectra and in the spectral dependence of ρ in the energy region below 2. 5 eV. However, contrary to the steady state excitation condition, the difference in ρ for the two kinds of samples is very large over the all spectral region investigated for the small values of the delay time. Taking into account the very broad lifetimes distribution of the red photoluminescence band, the effect of the ρ enhancement is much more pronounced for the photorecombination with short lifetimes.



Figure 2. Time-resolved PL and ρ spectra of porous Si prepared with polarized (solid line) and unpolarized light (broken line). Δt - delay time in respect to the laser pulse.

The increase of ρ might be attributed to the increase of the shape anisotropy in the system of porous silicon microcrystallites. The parameters of this anisotropy for the samples prepared with polarized and unpolarized light have been identified from the dependence of ρ versus orientation of exciting light polarization in the sample plane (Fig. 3). Here φ is the angle between



Figure 3. Angle dependence of the polarization level of PL (a) and dependence of ρ versus orientation of exciting light polarization in the sample plane (b). Angle between polarization direction of exciting light Θ , of detected light (φ) and that of the light, used during etching process.

the polarization vector of detected photoluminescence and that of the assisted light. (Θ) is the angle between polarization direction of excited light and that of the assisted one. For the samples prepared with both, unpolarized and polarized light there is a linear dependence between φ and Θ (Fig. 3a). It means that the preferential direction of photoluminescence polarization follows the polarization direction of excited light. This result is in agreement with previous observation for the ordinary p-type porous silicon^[1]. The polarization level for the samples prepared with randomly polarized light does not depend on the polarization direction of the excited light in the sample plane. Contrary, the samples prepared with linearly polarized light demonstrate well-defined angle distribution of ρ (Fig. 3b.). This discrepancy means that there is a specific direction of the optical anisotropy in the sample plane. The minima in the angle distribution of ρ coincide with the polarization direction of the assisted light and position of the minima is independent from the orientation of the crystalline silizium axes.

The electrochemical etching procedure is believed to create microcrystalls with the different shapes and orientations. For the n-type material the light assistance is essential for the generation of nonequilibrium holes^[5]. At the randomly polarized light the microcrystallites will preferentially absorb the of light with the direction of the electric field coinciding with the direction of the longer axes. Thus, these selforganizing etching conditions could stimulate the shape isotropisation in the system of microcrystallites. The spherisity of particles should not give rise to the high level of the photoluminescence polarization (Fig. 1).

Contrary, the linearly polarized light used under anodization induces the anisotropy of crystallite's shapes and orientations. The preferential absorption (in the direction of the electric field of the assisted light) will affect the further etching step mostly for the crystallites with the longest sizes in this direction. This process will smoothly deviate the parameters of the shape's anisotropy (ratio of the long to the short axis lengths) according to the angle distribution of the electric field intensity of the assisted light. As a result, the maximum of the anisotropy is expected to be in the direction perpendicular to the polarization of the assisted light. The angle distribution of the photoluminescence polarization level in the sample plane should simply follow the shapes and orientations distribution of the microcrystallites (Fig. 3b). In contrast to the isotropic system the contribution of crystallite shape anisotropy (projections on the axis related to the polarization of the assisted light) leads to the enhancement of the polarization level even for the direction with the minimum crystalline shape anisotropy (Fig. 1, Fig. 3b).

The presently observed anisotropy in the sample plane has a good agreement with the numerical calculation for Si ellipsoids in SiO₂ matrix^[6] and with the model of dielectric object with axial asymmetry^[7].

In conclusion we would like to emphasize the observation of the enhancement of polarization degree of n-type porous silicon photoluminescence. The optical anisotropy of the porous silicon in the sample plane was created by anodization of the silicon with linearly polarized light assistance.

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