Anisotropic polarization memory in thermally oxidized porous silicon

Hideki Koyama[a)]
Department of Practical Life Studies, Hyogo University of Teacher Education, Yashiro, Hyogo 673-1494, Japan

Philippe M. Fauchet
Department of Electrical and Computer Engineering, University of Rochester, Rochester, New York 14627

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Visible photoluminescence (PL) from thermally oxidized porous silicon (PSi) has been investigated in terms of polarization memory (PM). The PSi samples were prepared by anodization of $(100)p^+$-Si wafers in a HF/ethanol solution, followed by thermal oxidation at 700–1000 °C. These oxidized PSi samples show significantly anisotropic PM which depends largely on the polarization direction of the excitation light with respect to their crystallographic axes. In addition, the anisotropic PM from samples oxidized at 800 and 900 °C shows an anomalous emission-energy dependence. It is also observed that thermal oxidation at 1000 °C results in a significant decrease in the degree of PM, although it increases with increasing oxidation temperatures for ⩽900 °C. These experimental results suggest that the PL from oxidized PSi cannot be explained as a simple extension of the PL from as-anodized PSi and should be attributed to several different origins.
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A great deal of research interest is currently being focused on luminescent porous silicon (PSi) made by electrochemical anodization of Si wafers in HF solutions.[1] Light-emitting diodes (LEDs) based on this material benefit from a higher compatibility with the Si device-integration technology as demonstrated recently.[2] The external quantum efficiency of PSi-based LEDs has been improved to ~1%.[3] A significant increase in the electroluminescence efficiency of Er-doped PSi has also been achieved.[4] Multilayer optical reflectors/filters[5,6] and optical waveguides[7] are among other novel applications of PSi.

Practical applications of as-anodized PSi are rather limited by its emission instability due to imperfect oxidation of surface Si–H bonds.[8] Thermally oxidized PSi, which shows similar photoluminescence (PL) with a remarkably high stability,[9–13] is therefore more useful in device applications. However, the luminescence mechanism of oxidized PSi is still a matter of much debate. Quantum-sized Si nanocrystallites covered with a SiO_2 layer[9,10] or oxide-related defects[11,12] are suggested as the origin of the visible luminescence.

In the present study, we have investigated the visible PL from oxidized PSi in terms of polarization memory (PM).[14–19] The degree of PM is a measure of how perfectly the linear polarization of the excitation light is preserved in the emission. PM is a result of radiative recombination of electron-hole pairs localized such that their emission dipoles are not significantly changed from respective absorption ones.[14–16] Such localization can occur in nanocrystallites with anisotropic energy states due, for example, to their geometrical shapes.[16–19] PL from defect states with low point symmetry can also show a high degree of PM.[14,15]

The PSi samples were prepared by anodization of $(100)p^+$-Si wafers (0.008–0.012 Ω cm) in a solution of 50% HF:ethanol = 2:3 at a current density of 100 mA/cm^2 for 2.5 min. These samples were then oxidized in a furnace at 700–1000 °C for 10 min in dry O_2 atmosphere. Since oxidized PSi exhibits a blue-green PL with a high degree of PM after prolonged exposure to air,[18] the PL measurements were carried out within a few days after oxidation. A linearly polarized 514.5 nm Ar^+ laser beam was used as the excitation light. The laser beam was incident normally onto the sample surface after passing through a half-wave plate used as a polarization rotator. The emitted light was collected through an analyzer placed slightly off the normal direction. The degree of PM is defined by $P=(I_\parallel - I_\perp)/(I_\parallel + I_\perp)$, where $I_\parallel$ and $I_\perp$ are the intensities of the PL components polarized parallel and perpendicular, respectively, to the polarization direction of the excitation light. In order to cancel out the polarization-dependent response of the monochromator, the polarization direction of the excitation light was changed instead of rotating the analyzer to measure $I_\parallel$ and $I_\perp$.[16] A Si diode-array detector was used in the measurements of PM. PL spectra were measured using a cooled Ge detector and a lock-in technique. All the PL spectra were corrected for the spectral response of the apparatus.

Figure 1 shows the PL spectra of as-anodized and oxidized samples. The PL spectra of the oxidized samples have a similar peak position and broadening to the as-anodized one, except for the interference fringes due to an increased transmittance of the PSi layer after oxidation. The PL intensity increases with increasing oxidation temperatures up to 900 °C, beyond which it shows a decrease. The oxidation temperature at which the PL intensity becomes maximum is slightly higher than that reported in PSi samples made from p^- substrates.[9]

The degree of PM in the sample oxidized at 900 °C is shown in Fig. 2 as a function of the angle between the polarization direction of the excitation light and the [010] axis of the sample. A remarkable crystal-orientation dependence

a)Electronic mail: koyama@life.hyogo-u.ac.jp

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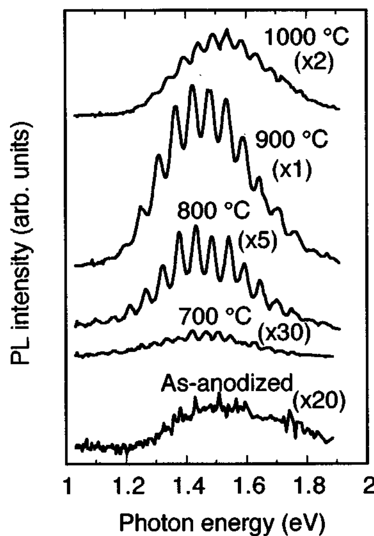

FIG. 1. PL spectra of as-anodized and oxidized PSi samples.

is observed. Besides, the anisotropy depends on the emission photon energy: the emission at 1.4 eV shows a larger degree of PM when the excitation light is polarized parallel to the ⟨110⟩ axes, while the emission at 1.8 eV shows maxima when the excitation light is polarized parallel to the ⟨100⟩ axes. No anisotropy in PM was observed in as-anodized samples.

Figure 3 shows the emission-energy dependence of the degree of PM in five PSi samples oxidized at different temperatures. It is clearly seen that the samples oxidized at 800 and 900 °C show an anomalous emission-energy dependence of PM at higher emission energies ($\geqslant$1.7 eV) the degree of PM is higher when the excitation light is polarized along the ⟨100⟩ directions, while at lower emission energies ($\leqslant$1.6 eV) it is higher when the polarization is in the ⟨110⟩ directions. In the samples oxidized at 700 and 1000 °C, however, only the latter anisotropy is observed. The degree of PM increases with increasing oxidation temperatures up to 900 °C, beyond which the PL becomes significantly depolarized. The sample oxidized at 1000 °C shows a degree of PM even lower than that of the as-anodized sample for photon energies $>$1.6 eV.

The anomalous emission-energy dependence of the anisotropy in PM can be explained on the basis of at least two different emission components:[20] a lower-energy emission which shows a maximum PM when the excitation light is polarized along the ⟨110⟩ axes and a higher-energy emission which shows a maximum PM when the excitation light is polarized along the ⟨100⟩ axes. These two emission components should be originating from Si crystallites or Si/SiO_2 interfaces, since the PM of these emissions has a clear crystal-orientation dependence. Also, another emission component is likely to be present. The third emission component may exhibit a very low PM, appear in samples oxidized at temperatures higher than 900 °C, and be responsible for the decrease in the degree of PM in the sample oxidized at 1000 °C.

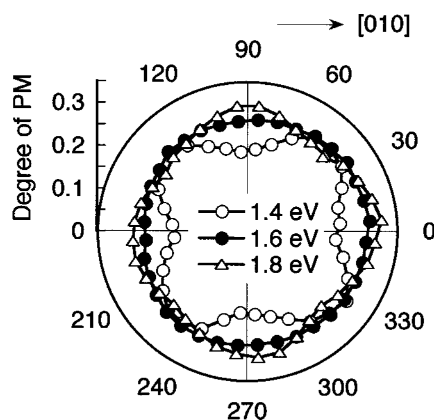

FIG. 2. The degree of PM in the PSi sample oxidized at 900 °C, plotted as a function of the angle between the [010] axis of the substrate and the polarization direction of the excitation light.

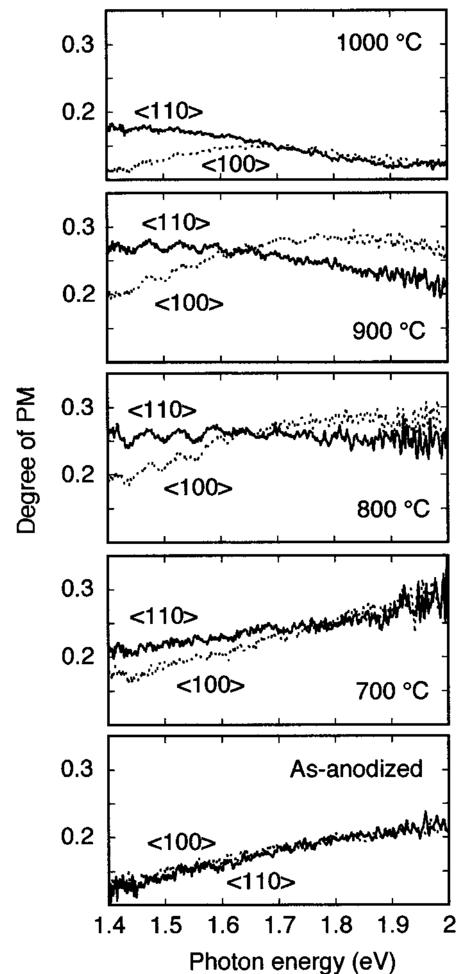

FIG. 3. The emission-energy dependence of the degree of PM for the five PSi samples of Fig. 1. The excitation light is polarized either along the ⟨100⟩ or ⟨110⟩ axes.

Kovalev *et al.*[19] have observed an anisotropic PM in as-anodized PSi under resonant photoexcitation. The anisotropy is such that the maxima of the degree of PM are observed when the excitation light is polarized parallel to the ⟨110⟩ axes. They explained this observation by higher photoexcitation probabilities of crystallites elongated in the ⟨110⟩ directions, because these crystallites were expected to have lower band gap energies due to anisotropy in the heavy hole effective mass. This effect, however, should be observed only at emission energies very close to the excitation energy, since the anisotropy in the hole effective mass does not affect the higher energy states.[19] Indeed, Kovalev *et al.*[19] did not observe any anisotropy in PM under nonresonant Ar^+-laser excitation.

According to Irene *et al.*,[21] the thermal oxidation rates of crystalline Si along the ⟨110⟩ and ⟨111⟩ directions are higher than that along the ⟨100⟩ directions. If this is the case also in the nanostructures of PSi, thermal oxidation should produce more Si nanocrystals elongated in the ⟨100⟩ directions. This can result in an anisotropic PM that shows maxima when the excitation light is polarized in the ⟨100⟩ directions. In addition, the oxide layers formed on the surface of the Si nanocrystallites reduce the hopping probability of carriers among them, leading to some enhancement of the degree of PM. This model, therefore, can explain the behavior of the higher energy emission component observed in the samples oxidized at 800 and 900 °C.

Several studies have suggested nonbridging oxygen hole centers (NBOHCs) as a possible origin for the visible PL from oxidized PSi.[12] The PM of the luminescence from NBOHCs in amorphous SiO_2 has been studied by Skuja.[15] Under Ar^+-laser excitation, these centers exhibit a broad PL in the photon-energy range between 1.6 and 2.4 eV, with a maximum at around 2.1 eV. Its degree of PM shows a relatively sharp decrease of $\sim -0.25\ eV^{-1}$ with decreasing emission photon energies. This emission energy range is similar to that of our higher energy emission component. However, the behavior of PM as a function of the emission photon energy is clearly different from our results shown in Fig. 3.

In conclusion, we have measured the polarization properties of the visible PL from thermally oxidized PSi. A significant anisotropy in PM is observed in all samples oxidized at 700–1000 °C. In addition, samples oxidized at 800 and 900 °C show an anomalous emission-energy dependence of the anisotropy: for emission energies $\leqslant 1.6$ eV the degree of PM reaches maxima when the excitation light is polarized parallel to the ⟨110⟩ axes, while for higher emission energies it shows maxima when the excitation light is polarized parallel to the ⟨100⟩ axes. The degree of PM increases with increasing oxidation temperatures up to 900 °C. Oxidation at 1000 °C, however, results in a remarkable decrease in the degree of PM. These results suggest that the emission from thermally oxidized PSi samples is composed of several different components originating from different mechanisms. Although the microscopic origins of these emission components are left unresolved, our experimental results show that the PL from thermally oxidized PSi cannot be described as a simple extension of the PL from as-anodized PSi.

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