Polarization Memory of Blue and Red Luminescence from Nanocrystalline Porous Silicon Treated by High-Pressure Water Vapor Annealing

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Abstract

The polarization memory (PM) effect in the blue and red photoluminescence (PL) of p-type porous Si (PS) treated by high-pressure water vapor annealing (HWA) has been investigated. HWA induces a significant blue PL emission at about 450 nm, together with a drastic enhancement of the red PL intensity. The polarization memory of the red emission band is anisotropic and is in agreement with emission from quantum sized Si nanocrystals, whereas that of the blue band is high and isotropic, indicating an emission mechanism related to localized states in the amorphous Si oxide surrounding the Si skeleton of the PS layer after HWA. HWA does not induce any blue emission in PS that was electrochemically oxidized (ECO) beforehand because the electrochemically grown oxide tends to prevent the formation of blue-emitting amorphous oxide upon HWA. The PM of ECO-PS at low emission energies is anisotropic, but in a direction 45° rotated compared to that of PS treated by HWA. This unique behavior may be related to the electrical nature of electrochemical oxidation. HWA increases the PM of ECO-PS. This could be attributed to the enhanced passivation induced by HWA.

Keywords:
434: Silicon
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262: Luminescence,
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Introduction

Nanocrystalline porous silicon (PS) is very attractive for optoelectronic applications [1-3] because of its tunable optical properties and its luminescence [4]. PS whose surface is kept oxygen-free can emit light from red to blue, as a result of quantum confinement and size effect. However, oxygen contamination of PS introduces levels in the gap that prevent emission of green and blue light [5]. Mere exposition to air for a few seconds is enough to suppress green and blue emission from PS. Therefore, stable blue photoluminescence (PL) from PS is difficult to achieve. Nevertheless, low efficiency blue luminescence is sometimes observed in oxidized or aged PS samples. The origin of this luminescence is not clear and has been attributed to various phenomena, such as oxide-related defects [6], contamination by carbonyl groups [7] and some kind of nanostructures [8].

Recently, we have been able to prepare PS layers emitting red luminescence very efficiently (23 % of external quantum efficiency at room temperature) by using high-pressure water vapor annealing (HWA) [9,10]. In addition, both PL and electroluminescence [1] have been completely stabilized by HWA, which provides a high-quality passivating thin oxide surrounding the nanocrystalline Si dots [9,10].

Under appropriate experimental conditions of HWA, a relatively efficient blue luminescence band can also be generated in PS, coexisting with the conventional red luminescence band. In this paper, the blue and red emissions from HWA-treated PS are studied by using PL and polarization memory (PM) experiments.

Experiments

The substrates used are B-doped p-type, (100)-oriented, and 4 Ω.cm silicon wafers with an Al back contact. PS layers of porosity 68% were formed by anodization in a solution of HF (55wt.%):ethanol= 1:1 at a constant current density of 50 mA/cm². PS thickness was 10 μm. The PS layers were rinsed with ethanol for 2 min. Some samples (named ECO-PS) were electrochemically oxidized under 50 mA.cm⁻², in H₂SO₄ (1M). The electrochemical oxidation (ECO) was stopped when the potential of the Si substrate versus the Pt electrode suddenly accelerated and exceeded 2 V, as previously described [11]. The ECO-PS layers were then rinsed with ethanol for 2 min and dried under N₂ flow.

For HWA [9,10], PS and ECO-PS samples were placed into a container with a certain quantity of de-ionized water at room temperature. The closed container was heated up to a temperature of 260°C, kept for 3 h, and then cooled down to room temperature. The water vapor pressure in the container was estimated using the Van der Walls equation for water. It was varied from 1.3 to 3.9 MPa. PS and ECO-PS treated by HWA are named HWA-PS and HWA-ECO-PS, respectively.

PM spectra were measured using a fiber-optic spectrometer (Ocean Optics USB 2000). The excitation source was a laser diode emitting at 3.02 eV, allowing PL detection below 2.8 eV. PL spectra were measured either using the 325 nm line of a He-Cd laser (allowing PL detection below 3.2 eV) or the same setup as for PM experiments. All measurements were performed at room temperature in air.

The degree of PM is defined as $P = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$, where $I_\parallel$ and $I_\perp$ are the emission components polarized parallel and perpendicular to the polarization direction of the excitation light, respectively.

Results and discussion

- As-anodized porous Si
Figure 1 shows PL spectra for various porous layers. As-anodized PS exhibits weak PL in the range 1.3-2 eV. Its shape is typical of the luminescence of the red band of PS [4], reflecting a distribution of size of Si nanocrystals. This PL intensity is very much enhanced by HWA at 1.3 MPa as expected from previous results [9,10]. In addition, a new emission band (blue band) appears in the range 2.3-2.8 eV. In order to investigate the effect of the pressure on the luminescence, a similar sample has been subjected to HWA at 3.9 MPa (Figure 2). Its PL was measured with a HeCd laser in order to get the PL spectrum up to 3.2 eV. In this case, the blue band is much more intense than for 1.3 MPa and appears peaked at about 2.8 eV (blue emission). The overall spectrum is well described as the sum of two Gaussian functions.

HWA oxidizes PS, and typically the higher the pressure, the higher the resulting oxidation level of PS [9,10]. Therefore, the pressure of 3.9 MPa leads to a more oxidized PS layer than the pressure of 1.3 MPa. The study of several samples has shown that the intensity of the blue band is correlated to the amount of oxide in PS. TEM experiments performed on Si nanowires treated by HWA have shown that the oxide induced by HWA is amorphous [12]. Furthermore, the emission peak (2.8 eV) is independent of the PS formation conditions and subsequent treatments (not the case for the red band). This result rules out the direct involvement of any size-dependent quantum confinement effect in the blue band emission. Rather, it suggests that the origin of this band in PS is related to localized states in the amorphous oxide surrounding the Si nanocrystals.

In order to get additional information on the two emission bands, PM experiments have been performed. PS can be regarded as an ensemble of differently oriented dipoles. Dipoles oriented parallel to the exciting polarization are preferentially excited and subsequently preferentially radiate in the excitation polarization [4]. In Fig. 3, the degree of PM of the HWA-PS sample shown in Fig. 1 is presented for several different emission photon energies as a function of the direction of $E_{EXC}$ (The vector electric field of the excitation light). The radial coordinate shows the values of $P$, and $\theta$ is the angle between $E_{EXC}$ and the [011] axis of the substrate.

The red band (1.5-2.2 eV) is significantly anisotropic. In general, as-anodized nano-PS exhibits isotropic PM [13-15]. However, PS prepared from heavily doped Si, typically exhibiting structural anisotropy, presents the same type of anisotropy as that shown here for HWA-PS, only when it is thermally oxidized in dry oxygen [15]. In our case, the Si substrate is lightly doped, and is less likely to lead to any structural anisotropy of the porous layer. Nevertheless, our results show that HWA does induce some kind of structural anisotropy in p-type PS, similarly to what thermal oxidation does in p'-type PS.

The nanostructures of luminescent as-anodized PS (with high porosity) and HWA-PS (with low initial porosity of 68%) are probably very different. The luminescent part of the nanostructure of as-anodized PS is mostly isotropic [13-15]. In contrast, ours results show that HWA-PS exhibits a markedly anisotropic nanostructure in the regions emitting at low energies. In our case, the initial PL of PS is very weak. HWA induces new luminescent nanocrystals due to size reduction and enhanced passivation. HWA may also induce the anisotropy observed at low emission energies, in the largest luminescent nanocrystals, if those regions, initially non luminescent, were anisotropic (maybe due to the nature of the PS formation mechanism itself) before HWA.

The blue band (2.3-2.7 eV) is isotropic. In addition, its degree of PM is very large, as also shown in Fig. 4. The blue-green emission (“fast band emission”) sometimes observed in thermally oxidized PS also exhibits a very large PM [8]. Thus, the emission of the blue band is most likely related to defects [6] or nanostructures [8,16] in the oxide.
As seen in Fig. 1, the PL of the red band is enhanced by ECO. This result has been attributed to enhanced carrier localization as well as size reduction quantum effects [17]. HWA further enhances the PL efficiency of ECO-PS (Fig. 1). This confirms our previous results [10,11]. However, the blue band observed in HWA-PS is not present in the PL of HWA-ECO-PS. By increasing the pressure, only a very weak emission of the blue band can sometimes be obtained. The difference with as-anodized PS is the amount of oxide generated by HWA and the final structure of the porous layer. Indeed, we have shown previously that the thin oxide layer generated by ECO at the surface of PS tends to hinder the oxidation induced by HWA. Thus, HWA induces less oxide in ECO-PS than in PS [10,11].

In order to better understand the effect of ECO and HWA on the PL, PM experiments were conducted on ECO-PS and HWA-ECO-PS. Figure 5 shows the PM results for ECO-PS. For emission energies below 1.6 eV, ECO-PS shows anisotropy that is different from that of HWA-PS (Fig. 3) and thermally oxidized PS [15]. Indeed, the degree of PM reaches its maximum when $E_{\text{exc}} || <100>$ and minimum when $E_{\text{exc}} || <110>$. For emission energies between 1.7 to 1.9 eV, the PM appears isotropic whereas above 2 eV, it is again slightly anisotropic, but this time the degree of PM is maximum when $E_{\text{exc}} || <110>$. ECO has induced a dramatic change in the PM at low energies. The porous nanostructure has probably been significantly modified. The shape of the large Si nanocrystals (emitting at low energies) is typically elongated in the <110> direction in HWA-PS (Fig. 3) and thermally oxidized PS [15]. In ECO-PS this direction is <100>. This type of anisotropy is unique. It may be explained by the way the ECO takes place. The mechanism of ECO of PS has been described in previous reports [17,18]. As it is electrical in nature, the holes flow through the most accessible energetic paths in the PS nanostructure, leading to preferential oxidation of its coarser parts. The process ends when the electrical contact between the PS layer and the substrate is broken by the grown oxide. As a result, the most significantly modified Si nanocrystals are the larger ones (emitting at low energies, or too large to emit light efficiently). This could explain why the PM spectra are significantly modified for the emission at low energies.

The mechanism leading to the PM anisotropy at low emission energies by ECO might be the following. On one hand, the nanocrystals emitting initially at a given energy will emit at a higher energy after ECO due to size shrinking, and may loose or somewhat keep their anisotropy (The emission in the range 1.7-1.8 eV is isotropic whereas above 1.9 eV, it is slightly anisotropic). On the other hand, some nanocrystals initially too big to emit any light could become emissive after ECO. These nanocrystals could be oriented differently from the quantum confined ones in the initial stage (maybe due to the nature of the PS formation mechanism itself), leading to the apparent anisotropy for the emission at low energies after ECO.

The reason for the difference in anisotropy between HWA-PS and ECO-PS is unclear. There are two main differences between the two treatments. On one hand, HWA oxidizes PS much more than ECO does. On another hand, ECO is electrical in nature and may modify the PS nanostructure differently compared to how HWA does.

Figure 6 shows the effect of HWA on the PM of ECO-PS. The original anisotropy of ECO-PS is kept by HWA. This is because the additional oxidation induced by HWA is not high enough to change significantly the already partially oxidized porous structure. The degree of PM significantly increases after HWA. We have previously shown that HWA dramatically reduces the defect density in PS. Therefore, the number of radiative transitions mediated by surface states may be significantly reduced in HWA-ECO-PS compared to that
in ECO-PS. Thus the number of radiative transitions involving only quantum levels in Si nanocrystals may be very much increased, inducing the increase in PM.

**Conclusion**

For p-type PS, in addition to enhancing the red PL band, the HWA treatment induces a significant blue PL emission peaked at about 450 nm. The PM experiments suggest that (i) the red emission band originates from radiative recombination of excitons in Si nanocrystals; (ii) the blue band may be related to localized states in the amorphous Si oxide induced by HWA in the PS layers.

For p-type PS that was electrochemically oxidized beforehand, HWA also enhances the red PL band. However, it does not induce any significant blue emission because the electrochemically grown oxide acts against further oxidation by HWA. The anisotropy of the PM of the PL of ECO-PS at low energies is different from that of HWA-PS. This behavior could be related to the electrical nature of ECO, acting on the nanocrystals geometry. The results also suggest an enhanced Si surface passivation by HWA.

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References

Figure captions

Fig. 1: PL spectra of as-anodized PS and ECO-PS, before and after HWA at 1.3 MPa.

Fig. 2: PL intensity of a PS sample treated by HWA at 3.9 MPa. The sum of two Gaussians was used to fit the spectrum.

Fig. 3: Degree of PM for the HWA-treated sample shown in Fig. 1, for several different emission photon energies as a function of the direction of $E_{\text{EXC}}$. The radial coordinate shows the values of P, and $\theta$ is the angle between $E_{\text{EXC}}$ and the [011] axis of the substrate.

Fig. 4: PL spectrum and P for two directions of the excitation polarization, for the HWA-treated sample shown in Fig. 1.

Fig. 5: Degree of PM for the ECO-treated sample shown in Fig. 1, for several different emission photon energies as a function of the direction of $E_{\text{EXC}}$. The radial coordinate shows the values of P, and $\theta$ is the angle between $E_{\text{EXC}}$ and the [011] axis of the substrate.

Fig. 6: Effect of HWA on the degree of PM for the ECO-treated sample shown in Fig. 1.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6