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LETTER TO THE EDITOR

Dynamics of the degradation by photo-oxidation of porous silicon: FTPL and FTIR absorption study

G Mauckner, K Thonke and R Sauer
Abteilung Halbleiterphysik, Universität Ulm, 7900 Ulm, Federal Republic of Germany

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Abstract. Fourier transform photoluminescence (FTPL) and Fourier transform infrared (FTIR) spectroscopy have been performed *in situ* during etching and on freshly anodized porous silicon after etching. During etching we find a continuous increase of Si–H bonds and no additional oxygen species at the inner surface of porous silicon. Other recent work has shown that freshly etched microporous silicon in oxygen ambient is subject to aging by oxidation. We demonstrate that photoirradiation in oxygen ambient causes photo-oxidation at the inner surface and thus accelerates aging significantly. Furthermore, we investigate the influence of different ambients and varying laser power on the dynamic process of PL degradation of, and increasing oxygen incorporation into, freshly etched porous silicon. We observe a rapidly decreasing PL intensity accompanied by PL peak blue shifts up to 200 meV.

The observation of efficient visible light emission at room temperature from porous silicon has begun to revitalize silicon as a prospective optoelectronic material [1,2]. However, anodized porous silicon suffers from the instability of photoluminescence (PL) in oxygen ambient under illumination and humidity [3]. By SIMS analysis, it has been shown that storage of porous silicon in air for about one year leads to a large increase in the oxygen content and other impurities [4]. This aging process, identified as oxidation, is accompanied by a reduction in the PL intensity. In contrast, the PL intensity is increased for electrochemical oxidation under anodic bias [5,6]. Recently it has been shown that thermal oxidation of porous silicon strongly quenches the emission intensity and shifts the PL spectra to higher energies [7]. However, the PL can be recovered by thermal oxidation at temperatures above 700 °C [8].

Understanding the luminescence mechanism and determining the sources of degradation is obviously of critical importance for any potential device application. In this letter we present an optical *in situ* study of porous silicon during preparation as well as in its freshly prepared state. To investigate the chemical composition of porous silicon during and after anodic etching, we use Fourier transform infrared (FTIR) absorption spectroscopy. Fourier transform photoluminescence (FTPL) spectroscopy was used to investigate the dynamic process of PL intensity degradation and stabilization of freshly porous silicon during light irradiation in air and nitrogen ambient.

The substrates used were boron-doped p^--Si (100) wafers with resistivities of 10 Ω cm. Square samples (25×25 mm^2) were cut from wafers and were electrochemically anodized in a double Teflon cell, similar to that described by

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Zorinski *et al* [9]. In addition, our electrochemical cell is equipped with optical calcium fluoride windows parallel to the front and back edges of the Si substrate to allow optical *in situ* experiments during anodic etching. The anodization was done under dark conditions with current densities in the range 10–80 mA cm^{-2} in 2:1 (Merck HF Selectipur (50%), Ethanol Merck Selectipur) electrolyte for 1–30 min and was continuously stirred by a magnetic stirrer. After etching the samples are removed and immediately dried in a gas stream of N_2. The broad red PL bands seen for these samples typically peak at 1.7 eV ($\approx$ 730 nm wavelength) with linewidths of about 350 meV ($\approx$ 150 nm).

In FTIR absorption measurements the transmitted mid-IR light was analysed by a Bomem DA8 Fourier transform spectrometer equipped with a Globar (SiC) IR light source and a liquid-nitrogen-cooled mercury cadmium telluride photodetector. FTPL spectra were recorded using the blue 458 nm line of an argon ion laser for excitation and the Fourier spectrometer with a silicon photodiode as detector.

First we studied FTIR absorption spectra during sample preparation as previously described. Since ethanoic HF itself strongly absorbs mid-IR light, the electrolyte was drained for a short period (2 min) for recording the transmission spectra and then replaced again. During the absorption measurements the (porous) silicon surface was still covered by a thin ethanoic HF film providing protection against contamination with ambient air. For reference, transmission spectra of the Si substrate with and without electrolyte film were recorded. The next series of spectra was recorded after anodic etching with 35 mA cm^{-2} for periods of 1 min. After 5 min total etching time the electrolyte was removed and the sample was blown dry by nitrogen gas. Figures 1 and 2 show the absorption spectra of this sequence of anodic etching. Absorption peaks linked to the porous layer are observed as a triplet at 2085–2140 cm^{-1}. The other stronger absorption bands at 1000–1100 cm^{-1} and 1350–2000 cm^{-1} can be assigned to the electrolyte since they disappear after the sample has been dried in nitrogen. The 1100 cm^{-1} peak is due to an antisymmetric interstitial Si–O–Si stretching mode as typically observed in Czochralski (CZ) grown, oxygen-rich bulk silicon [10]. The triplet of absorption peaks at 2085 cm^{-1}, 2115 cm^{-1} and 2140 cm^{-1} has been assigned to Si–H_x (x = 1, 2, 3) stretching modes at the silicon surface and they are discussed in detail in [11, 12]. Freshly etched porous silicon covered with ethanoic HF, however, exhibits a line broadening for the Si–H_x peaks. This broadening can be attributed to the interaction of SiH vibrations with electrolyte molecules and gives clear evidence that these Si–H_x species are located at the surface of the porous silicon [13]. During anodic etching we observe a continuous increase of hydrogen concentration with etching time. This indicates the continuous growth with etching time of the internal surface where hydrogen is chemisorbed. After anodic etching and N_2 drying the hydrides in porous silicon are stable and no additional surface oxygen species at 1050–1150 cm^{-1} can be seen.

It is known that porous silicon, stored in air for days or weeks under dark conditions, slowly incorporates an increasing amount of oxygen [4]. In order to investigate the origin of aging, we exposed freshly anodized porous silicon to light immediately after etching. FTIR absorption spectroscopy shows that surface oxidation can be accelerated by light exposure. In a first series of experiments, we illuminated freshly etched porous silicon by an Ar ion laser beam of 458 nm wavelength with a power density of 1.5 mW mm^{-2}. Figures 3 and 4 show the resulting FTIR absorption spectra for exposure times of between 0 and 162 min. The broad Si–O vibrational band at 1100 cm^{-1} indicates the formation of silicon oxide on the

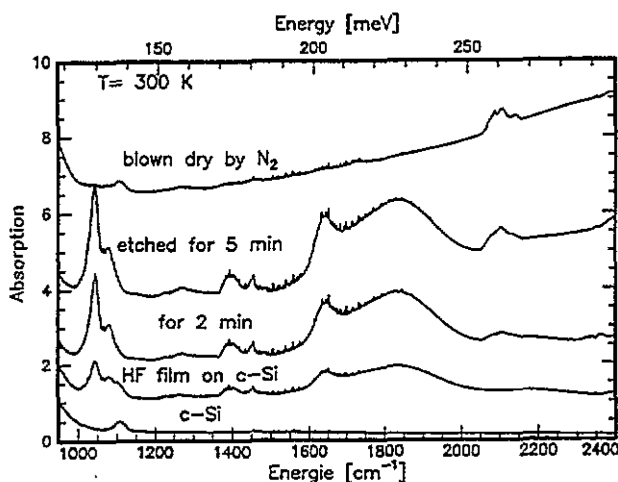

Figure 1. FTIR absorption spectra *in situ* during anodic etching: crystalline Si, electrolyte film (HF) on c-Si, after 2 and 5 min etching (35 mA cm^{-2}) and finally after 5 min etching and drying in nitrogen.

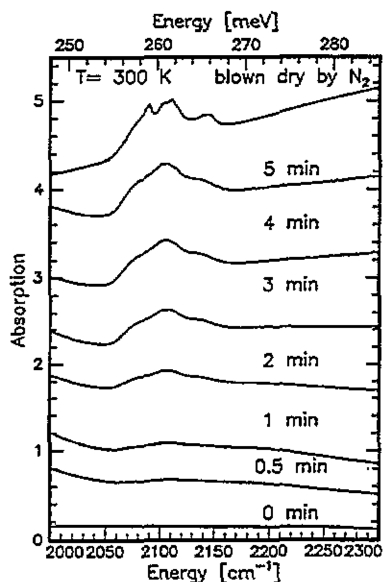

Figure 2. FTIR hydrogen triplet absorption bands Si–H$_x$ (x = 1, 2, 3) *in situ* during anodic etching for 0, 0.5, 1, 2, 3, 4 and 5 min etching time and after drying in nitrogen.

surface with increasing exposure time. In parallel, we notice the appearance of Si–O–H vibrational bands at 2200 cm^{-1} and 2250 cm^{-1}, which indicate the progress of oxidation by the introduction of an intermediate oxygen atom into the Si–H bonds. The photo-oxidation can be achieved using light in the visible region (vis) or ultraviolet (UV). Even IR exposure with 1.3 μm wavelength light leads to enhanced oxidation. Therefore, we assume an upper limit for the activation energy E_a of photo-oxidation in porous silicon of 0.95 eV. This value is close to the thermal activation energy of 0.60 eV for oxidation of porous silicon [12]. The integrated absorption for the Si–O peak at 1100 cm^{-1}, which is an estimate for the number of oxidized silicon atoms,

is approximately proportional to the square root of the exposure time, similar to room-temperature oxide growth on α-Si:H [14]. This suggests that a diffusion-limited process determines the oxidation kinetics. The hydride species seen at 916 cm^{-1}, 2085 cm^{-1} and 2250 cm^{-1} do not desorb during oxidation.

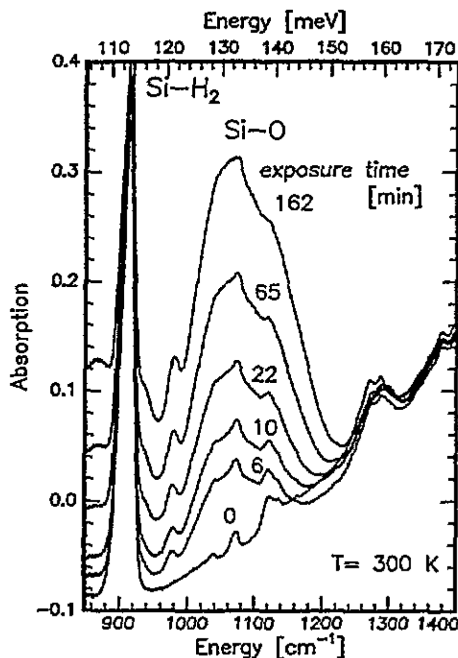

Figure 3. FTIR Si–O absorption band of freshly etched porous silicon (35 mA cm^{-2}, 20 min) after laser exposure for times between 0 and 162 min.

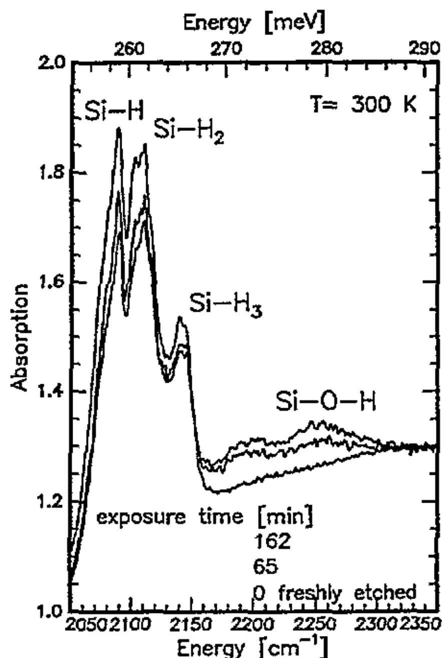

Figure 4. FTIR absorption peaks of Si–H_x (x = 1, 2, 3) and Si–O–H of freshly etched porous silicon (35 mA cm^{-2}, 20 min) after laser exposure for between 0 and 162 min.

Next we studied the PL degradation by laser irradiation in detail. The pumping laser beam at 458 nm acts simultaneously as an irradiation light source. FTPL is extraordinarily suitable for studying the dynamic behaviour of the *in situ* PL intensity, since data acquisition for recording PL spectra takes only a few seconds. Figure 5 shows the dynamic *in situ* PL degradation in air of fresh porous silicon etched with 35 mA cm^{-2} for 2 min. The PL intensity is reduced to 50% or less of its initial value after a few minutes and decreases to a quasi-stable level. Depending on the sample preparation we observe stabilization at 15–60% of the initial PL intensity level after 15–60 min. We observe sensitive dependence on ambient atmosphere and on the incident light power density. In nitrogen atmosphere the PL intensity stabilizes on a definitely higher intensity level in comparison with oxygen-containing ambients like air. This shows evidence for a surface oxidation process. A higher light power density on the sample makes no change in the final stabilized intensity level, but degradation is much faster.

The PL degradation is accompanied by clear PL peak shifts to higher energies by 200 meV (figure 6). Within the quantum size model [1, 2, 15] this blue shift can be understood by size reduction of silicon microcrystallites with increasing oxidation.

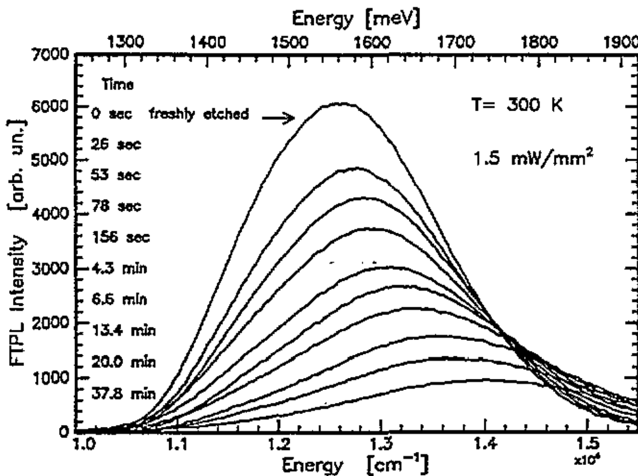

Figure 5. The dynamics of *in situ* PL degradation of freshly etched porous silicon ($35\ mA\ cm^{-2}$, 2 min) in air (laser wavelength 458 nm and power density $1.5\ mW\ mm^{-2}$).

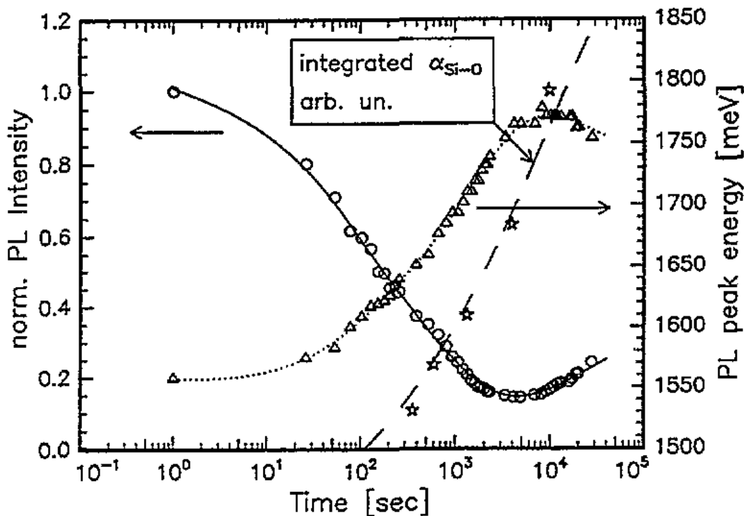

Figure 6. Dependence of the normalized PL intensity (solid line), PL peak shift (dotted line) and integrated absorption of the Si–O bands at $1100\ cm^{-1}$ (dashed line) of freshly etched porous silicon ($35\ mA\ cm^{-2}$, 2 min) in air on the laser exposure time (laser wavelength 458 nm and power density $1.5\ mW\ mm^{-2}$).

A similar quantitative energy shift to higher energies was also observed for thermal oxidation [7] as well as for anodic oxidation [5].

For long irradiation times (more than one hour) we observe in some samples a weak recovery of the PL intensity. Figure 6 also shows the dependence of the integrated absorption of the Si–O band at $1100\ cm^{-1}$, which is proportional to the oxygen concentration, on the laser exposure time. No simple correlation between oxygen concentration and the PL intensity or peak shift can be found. In order to

estimate radiative versus non-radiative recombination, we checked the luminescence efficiency of a degraded sample. The luminescence radiation of the sample, excited by the 458 nm laser line under well defined power density, was focused on a calibrated power meter. Taking account of the finite solid angle and the reflection losses of the mirror optics, we determined an approximate quantum efficiency of the order of 1%. Therefore we conclude that the dominant mechanism for recombination is non-radiative. Recently it was reported that when the hydrogen passivation is replaced by a high-quality thermal oxide, the PL is efficient again [8]. It was shown that the dangling-bond densities in thermally oxidized porous silicon have a strong influence on PL intensity. The chemical composition of the surface coverage, especially the oxygen content, seems to be only a minor factor in determining the PL intensity of porous silicon in air ambient. It seems likely to us that the microcrystallite size and densities of non-radiative defect centres are the main parameters in controlling PL properties. Further work is needed to clarify the details. Nevertheless it is useful to protect porous silicon from contamination with oxygen by a suitable cap layer to reach stable luminescence

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