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# Visible Luminescence from Porous Silicon and Siloxene

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### Abstract

Infrared transmission and Raman spectra of siloxene  $(Si_6O_3H_6)$  and porous Si have been analyzed in terms of the structural composition. Siloxene consists of  $Si_6$ -rings interconnected by oxygen and terminated by hydrogen, and corrugated Si(111)-planes saturated by OH and H. The pronounced photoluminescence of siloxene is mainly related to the Si<sub>6</sub>-rings. Porous Si shows similar luminescence and almost identical vibrational properties as siloxene, which makes this class of materials a possible candidate for the origin of the luminescence in p-Si. Annealing at temperatures below 300 °C and moderate illumination of siloxene induces the transformation from the Si-plane-like structure to the Si-ring-like structure. Anneal temperatures above 300 °C and intense illumination of both siloxene and p-Si leads to an effusion of hydrogen and an irreversible oxidation of the samples.

#### 1. Introduction

The recent discovery of highly-efficient, visible photoluminescence from so-called porous silicon [1, 2] has attracted much attention, in particular because of its potential application for an integration of light-emitting devices with conventional silicon-technology. Porous Si (p-Si) is obtained by anodic oxidation of crystalline silicon in an an  $HF/C_2H_5OH$  electrolyte. The exact structure of the resulting porous layer (Si-skeleton) depends on the concentration of free carriers (doped or optically excited), the current density used for anodic oxidation, and the composition of the electrolyte. Above a critical current density or below a critical HF concentration, electro-polishing of the Si-surface is observed instead of the formation of the porous layer [3]. Even though many groups have reproduced the preparation of the luminescent p-Si layers, the mechanism of the luminescence remains controversial. To shed some light on the origin of the luminescence in p-Si and to relate the luminescence in p-Si to other Si-based materials, we recorded the photoluminescence (PL) spectra of the various materials under identical experimental conditions (Fig. 1). In principle, many different luminescence mechanisms could be important in p-Si: localization of electron-hole pairs by disorder (as in amorphous hydrogenated silicon, a-Si:H), increased optical bandgap due to alloying (as in a-Si : O : H) or confinement in small crystallites (as in microcrystalline silicon,  $\mu$ c-Si). Compared to these PL intensities, however, the luminescence due to specific radiative centers in siloxene



Fig. 1. A comparison of the photoluminescence spectra of various siliconbased materials at 300 K (a) and 77 K (b)

 $(Si_6O_3H_6)$  is several orders of magnitude larger, and is the only example comparable to the one observed in p-Si (see Fig. 1). This pronounced luminescence behavior of siloxene and its chemical derivates has been known since 1922, [4-8] and siloxene is up to now the only silicon-related compound kown in the literature to exhibit such a strong room temperature luminescence.

To further investigate the structural properties of both, siloxene and p-Si, we performed Raman- and infrared-transmission (ir) measurements. Figure 2 compares the ir spectra of siloxene, p-Si, and an amorphous a-Si: O: H sample. The main absorption bands arising from vibrations



Fig. 2. Infrared absorption spectra of anodically oxidized porous silicon (solid line), siloxene (dashed line), and amorphous silicon alloy (dotted line).



Fig. 3. Infrared transmission spectra of siloxene at 300 K. The upper trace shows the spectrum of an as-prepared sample. The middle trace is the spectrum of a 200 °C-annealed sample. The spectrum at the bottom was obtained after illumination with ultraviolet light

of the various bonds in these materials are (see Figs 2 and 3): Si—Si  $(520 \text{ cm}^{-1})$ , Si—H  $(645 \text{ cm}^{-1}, 842 \text{ cm}^{-1}, 870 \text{ cm}^{-1}, 935 \text{ cm}^{-1}, 2100 \text{ cm}^{-1}, 2200 \text{ cm}^{-1} \text{ and } 2250 \text{ cm}^{-1})$ and O—H  $(1635 \text{ cm}^{-1} \text{ and } 3400 \text{ cm}^{-1})$ . The spectra of siloxene and p-Si are almost identical over the entire frequency range from 300 to  $4000 \text{ cm}^{-1}$ . The spectrum of a-Si : O : H, [9, 10] on the other hand, shows basically the same bands but in completely different relative intensities. We conclude therefore that similar bonding configurations must be present in p-Si and siloxene [11].

Siloxene is chemically synthesized from CaSi<sub>2</sub> in an HCl solution [4-8]. CaSi<sub>2</sub> consists of corrugated Si(111)-planes separated by Ca-layers. In the HCl solution, the Ca-layer is removed and the remaining Si-bonds are ideally saturated by H and OH. In reality, a small concentration of other bond terminators is also incorporated (e.g. Cl). Two different structural units of siloxene have been proposed: [4, 12] six-fold Si-rings (interconnected by O and terminated by H) [4], or Si-planes terminated by H and OH [12]. The relative amount of the two modifications found in a specific sample strongly depends on the experimental conditions used for the chemical processing. Raman spectra of the starting product, CaSi2, and the resulting siloxene samples (prepared according to Kautsky's recipe [4]) are compared to the spectra of p-Si in Fig. 4. All three materials show a prominent peak around 515-520 cm<sup>-1</sup>. Siloxene and CaSi<sub>2</sub> also show a second peak at  $\approx 380 \,\mathrm{cm}^{-1}$ . Since the only structural similarities between siloxene and CaSi<sub>2</sub> are the corrugated Si-planes, the modes around 380 cm<sup>-1</sup> and  $515 \text{ cm}^{-1}$  are assigned to Si-Si vibrations in these planes. To compare the Raman spectra of p-Si to  $\mu$ c-Si, we show results for  $\mu$ c-Si obtained by various groups in Fig. 5. Depending on the crystallite size, the Raman peaks shifts towards lower energies, correlated with a characteristic broadening of the mode [13, 14]. For the observed shift of



*Fig.* 4. Raman spectra of self-supporting anodically oxidized porous silicon, siloxene, and  $CaSi_2$ . The spectra were recorded under identical experimental conditions at 300 K with the 457.9 nm line of an Ar<sup>+</sup>-laser

about  $6 \text{ cm}^{-1}$  in p-Si, one would expect a broadening of at least  $15-20 \text{ cm}^{-1}$  for microcrystals. In contrast, the Raman line of both p-Si and siloxene are only broadened by about  $7 \text{ cm}^{-1}$ , incompatible with the assumption of microcrystals. Complementary to the ir measurements mentioned above, these Raman experiments give further evidence that the structural composition of p-Si and siloxene are similar [11, 15].



Fig. 5. Full-width at half-maximum  $\Gamma$  of the Raman peak vs. frequency shift  $\Delta \omega$  from the position in cristalline silicon. Small symbols are experimental data for  $\mu$ c-Si, large symbols those for porous silicon and siloxene. Dashed and dotted curves are theoretical calculations [13, 14]

Vibrational spectroscopy has in the past proven to be a powerful and sensitive tool for the investigation of bonding structures. As an example in the present context, we have recently reported on the change of the ir spectra of siloxene after a step-wise annealing of the samples between 100 °C and 500 °C [15]. The spectra for the as-prepared Kautskysiloxene and the 200 °C-annealed sample are shown in Fig. 3. After annealing, the sharp feature at  $520 \text{ cm}^{-1}$  and the 645 cm<sup>-1</sup>-mode almost disappear in the ir spectra, and the modes at  $460 \text{ cm}^{-1}$ ,  $845 \text{ cm}^{-1}$ ,  $870 \text{ cm}^{-1}$ , and  $2250 \text{ cm}^{-1}$ become stronger. Similar changes occur if the as-prepared sample is UV-irradiated in ambient atmosphere and at room temperature for one minute. Since the sharp feature at  $520 \,\mathrm{cm}^{-1}$  disappears in the annealed and illuminated samples, it cannot arise from oxygen-related vibrations. Instead, this mode can be assigned to the same origin as the corresponding mode in the Raman spectra [11, 15]: vibrations in the Si-planes of siloxene which become ir active due to a dipolemoment induced by the ligands. The increase of the intensity of the hydrogen stretching modes above  $2100 \,\mathrm{cm}^{-1}$  in the annealed and illuminated samples (due to Si-H vibrations with one or more oxygen atoms backbonded to the Si-atom) and the increase of the characteristic Si-O-Si vibration at 460 cm<sup>-1</sup> indicate an increase in the number of Si-O-Si bonds. This can be qualitatively understood in terms of the two structural models mentioned above which have been proposed for siloxene. The Si-plane structure for siloxene is metastable, and moderate annealing or illumination activates a restructuring without necessarily changing the chemical composition. Oxygen, which was part of the plane-terminating OH-groups, is inserted into the Si-planes and the planes are fragmented (the  $520 \,\mathrm{cm}^{-1}$ mode disappears in the i.r. spectra). At least part of the planes will be transformed by this process in the Si-ring structure, where six-fold Si-rings are connected by Si-O-Si bridges. This is consistent with an increase of the 460 cm<sup>-1</sup>mode.

The Si<sub>6</sub>-rings are a likely structure responsible for the luminescence in siloxene [11]. The process of forming Si<sub>6</sub>-rings from the Si-planes leads to a dramatic increase of the luminescence intensity by moderate annealing in the case of siloxene prepared according to the stringent recipe of Kautsky (which yields mostly Si-planes). Note that this is not the case for siloxene prepared according to Wöhler's recipe [6] and also for p-Si where oxygen is present in the chemical processing and where the Si<sub>6</sub>-rings are already formed in the as-prepared samples, without further annealing. In fact, as we will discuss below, the Si<sub>6</sub>-rings are not very stable against thermal treatment either, and can easily be destroyed by heating the samples, leading to a decrease in the observed luminescence.

If siloxene is annealed above 300 °C, hydrogen is quickly evolved (Fig. 6) leaving behind a substoichiometric  $SiO_x$ . The effusion curves of Fig. 6 were obtained by heating the samples in vacuum and measuring partial pressures by means of a mass spectrometer. In Fig. 6, porous Si shows qualitatively a similar behavior as siloxene, however with a more pronounced high-temperature hydrogen peak. This second peak in p-Si is most likely due to additional H passivating the surface of the remaining Si-skeleton.



Fig. 6. Effusion curves for anodically oxidized porous silicon and siloxene

In the same way as annealing above 300 °C, very intense illumination of siloxene (Fig. 7) destroys the luminescent siloxene structures, observable as the decrease of the  $485 \text{ cm}^{-1}$ -mode in the Raman spectra ascribed to the Si<sub>6</sub>-rings [15]. The destruction of the Si-rings, either by heating or by illumination, is accompanied by a drastic decrease of the visible luminescence. An additional contribution to the decrease of the luminescence caused by Hevolution is an increasing amount of Si-dangling bonds which act as non-radiative recombination centers. This is corroborated by spin resonance measurements.

So far we have concentrated on the properties of siloxene. We want to turn now to the corresponding properties of p-Si. Many groups have observed the influence of thermal treatment and laser irradiation on the PL of p-Si. In light of the structural changes observed in siloxene above, extreme



Fig. 7. Raman and photoluminescence spectra of (a) siloxene annealed to obtain red luminescence and (b) the same sample after intense laser illumination



Fig. 8. Luminescence intensity of anodically oxidized porous silicon at 300 K as a function of the incident laser intensity

care has to be taken not to change the structure of p-Si during the measurements. We have observed that even an unfocused laser beam with intensities of only 50 mW already changes the structure of p-Si. Thus, whenever luminescence intensites are reported in the literature, the results have to be handled with some care if high laser intensities have been used for the measurements. Figure 7 indicates that intense illumination of siloxene results not only in a decrease of the PL signal, but that due to the structural changes the characteristic wavelengths of the PL change, too. Similar effects are likely to occur in p-Si as well. The dependence of the observed PL intensity in p-Si at a fixed wavelength (750 nm) on the incident power is displayed in Fig. 8. Over several orders of magnitude the PL intensity is proportional to the incident laser power. Above about 1 mW/cm<sup>2</sup> the PL increases sublinearly. Studies of the photodegradation of p-Si in various gases [16] show that the degraded PL can be



Fig. 9. Temperature-dependence of the photoluminescence intensity in anodically oxidized porous silicon.  $I_0$  is the luminescence intensity at zero temperature,  $T_0 = 50$  K is a fit parameter in eq. (1)

partially recovered by either additional etching in HF or by moderate annealing. Assuming that the reduced PL intensity for high excitation intensities is a result of structural changes similar to the ones discussed in siloxene, the recovery of the PL by slight annealing can be understood in terms of the activated insertion of oxygen into the remaining Si-planes to create more  $Si_6$ -rings, leading to an increased PL intensity. This process, however, would not be repeatable indefinitely.

As a last remark, the temperature dependence of the luminescence in p-Si is compared to the one observed in amorphous a-Si : H. It is known that the luminescence behavior of various amorphous semiconductors can be described by the relation [17]:

$$\left(\frac{I(0)}{I(T)}-1\right) \propto \exp\left[\frac{T}{T_0}\right],$$
 (1)

where  $I_0$  is the extrapolated PL intensity at zero temperature and  $T_0$  is a fit parameter. In the case of a-Si: H samples e.g.,  $T_0$  is a well-defined constant of  $T_0 = 23$  K [17]. Fo p-Si, we find that an excellent fit to the experimental data over several orders of magnitude of the PL intensity is also possible by eq. (1) with  $T_0 = 50$  K. The physical origin of the temperature dependence of the luminescence in a-Si: H is usually explained in terms of excitation of electronhole pairs followed by thermalization and relaxation of carriers into exponential band tail states and subsequent recombination of these electron-hole pairs. It is known that siloxene has an exponential tail, too, so that a similar temperature dependence should be expected if siloxene is responsible for the PL in p-Si.

## 3. Conclusions

Infrared transmission and Raman spectra of siloxene and porous Si have been analyzed in terms of the structural composition. Siloxene is a mixture of Si<sub>6</sub>-rings interconnected by oxygen and terminated by hydrogen and corrugated Si(111)-planes saturated by OH and H. Annealing below about 300 °C and moderate illumination of siloxene activates the transformation from the Si-plane-like structure of the Si-ring-like structure. The pronounced photoluminescence of siloxene is mainly related to the Si<sub>6</sub>-rings. Porous Si shows similar luminescence and almost identical vibrational properties as siloxene, which makes this class of materials a possible candidate for the origin of the luminescence in p-Si. Anneal temperatures above 300 °C and intense illumination of both siloxene and p-Si leads to an effusion of hydrogen and an irreversible oxidation of the samples.

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