

Oxide-Stabilized Porous Silicon for Luminescence Applications

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By means of rapid-thermal oxidation we convert the hydrogen-passivated internal surfaces of porous Si to a stable device-grade oxide. The luminescence first quenches with rising process temperature. It recovers fully for temperatures where a good quality oxide is formed. A model explaining the luminescence is given. A narrow, green luminescence band with fast response ($\sim$ nsec) is discovered in the material oxidized above 1000°C.

INTRODUCTION

Electrochemically etched Si has remarkable optical properties in the visible spectrum. Lehmann et al. /1/ point out the blue-shifted onset of absorption for the hydrogen-passivated microporous Si. Canham /2/ emphasizes the luminescence in the visible. In various references the prospects for light-emitting devices based on porous Si (PS) have been discussed.

The stability of the PS is a problem. The internal, dihydride-covered surface of the as-etched material is unstable against oxidation at room temperature, against thermal decomposition and photolytic dissociation. As a result the luminescence intensity can be quenched. To overcome this difficulty we suggest replacing the hydride coverage by a device-grade thermal oxide /3/. Rapid thermal processing (RTO) is required to preserve the Si crystalline cores of the PS. Alternatively, as shown in ref./4/, one could start with large-size crystallites and use a furnace oxidation procedure.

SAMPLE PREPARATION

We start with (100)-oriented, p-type (0.07 and 5 Ω cm) Si wafers

electrochemically etched in 50% HF in ethyl alcohol (1:1 by volume). Currents are in the range 30-100 mA/cm². Layer thickness is 10 μ m. We use a commercial RTO apparatus (Heat Pulse 610) and process time of 30 s. The oxidation temperature is increased in steps of 100°C starting at 400°C and rising to 1200°C.

OPTICAL PROPERTIES OF RTO-PROCESSED PS

The most remarkable characteristic of the PS processed in dry oxygen is shown in Fig.1. The luminescence is first quenched, but with increased T_{ox} at 900°C the original intensity is fully recovered. This behavior is quite general and has by now been reproduced in many series /3/.

IR vibration spectroscopy shows that with successively increased T_{ox} the hydrogen originally present in PS is reduced while the amount of oxide monotonically rises. Luminescing material for $T_{ox} \geq 700^\circ\text{C}$ contains no detectable amounts of H bonded to Si. This agrees with the thermo-effusion experiments /5/. The IR spectra show a broad band of Si-Si vibrations centered at 470 cm⁻¹. This is evidence for disorder of the Si-Si bonds on the microcrystal surface.

Plotted also in Fig.1 is the spin-resonance intensity. The ESR signal has a maximum in the T_{ox} range where the luminescence is quenched. It practically vanishes at $T_{ox} \geq 800^\circ\text{C}$, where a good quality oxide is known to form on Si.

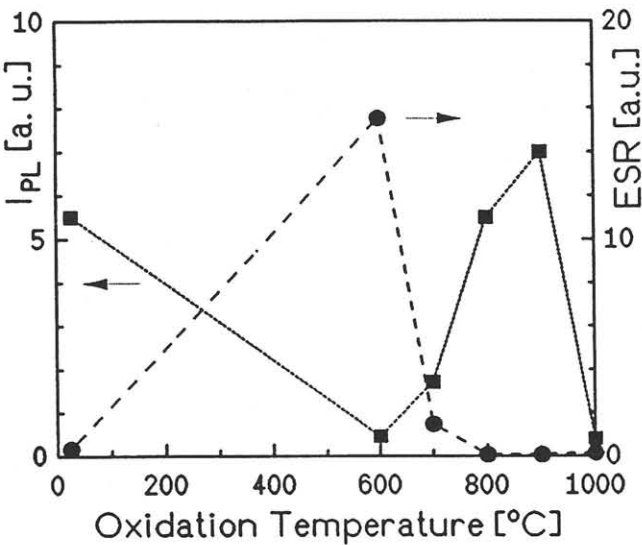


Fig.1 Photoluminescence intensity I_{PL} in arbitrary units for a series of 6 RTO-processed materials vs. the oxidation temperature (time 30 s). On a similarly processed wafer the electron spin resonance amplitude ESR is recorded. Note the maximum ESR at the 600°C position where I_{PL} has a minimum. The excitation wavelength is 353 nm.

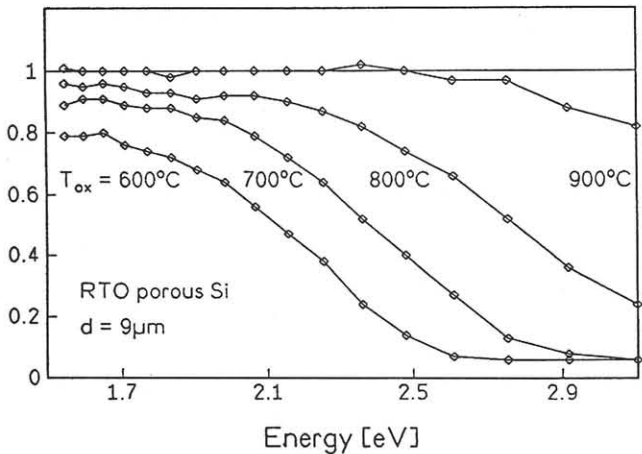


Fig.2 Relative transmission through $18\ \mu\text{m}$ of RTO-processed porous Si as a function of photon energy. The curves are normalized to transmission curves for 1000°C and above.

The vanishing of the luminescence for samples with $T_{ox}=1000^\circ\text{C}$ and above has an obvious explanation in terms of the curves in Fig.2. We show a relative transmission signal vs. photon energy. It is the intensity of light reflected at the PS-substrate boundary and having traversed twice the $9\ \mu\text{m}$ thick layer. The increased transparency at the energy of the PL exciting photon explains the luminescence decrease for high T_{ox} .

There is a consistent shifting of the luminescence peaks as we go through the T_{ox} series. Fig.3 shows that the initial oxidation is always accompanied by a shifting of the peak to lower energy. Above $T_{ox}=700^\circ\text{C}$, there is a blue-shift. The first effect shows that the nature of the chemical bonding on the crystallite surfaces influences the PL energy. With the increasing oxidation, particle sizes must reduce. This relates to the blue-shifting in Fig.3.

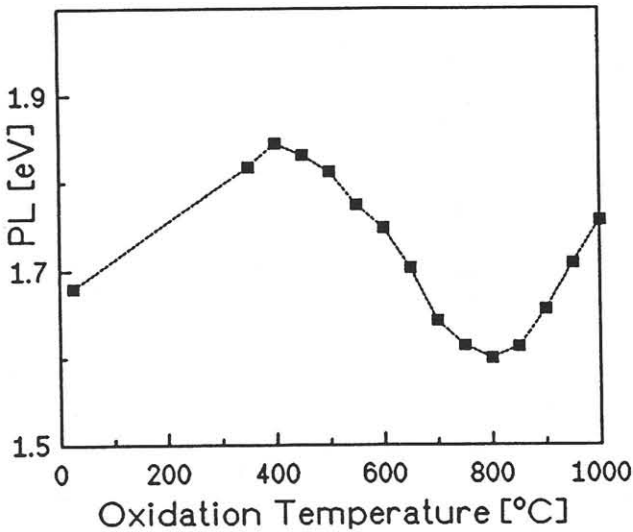


Fig.3 Position of the luminescence intensity maximum vs. process temperature.

At some particular value of T_{ox} (here 900°C) the spectra of the hydrided and oxidized materials are equal. We show how closely they are matched in Fig.4. The exciting new feature in Fig.4 is an intense green luminescence band at 2.3 eV seen for the $T_{ox}=1100$ and 1200°C materials after aging for a month or so. This

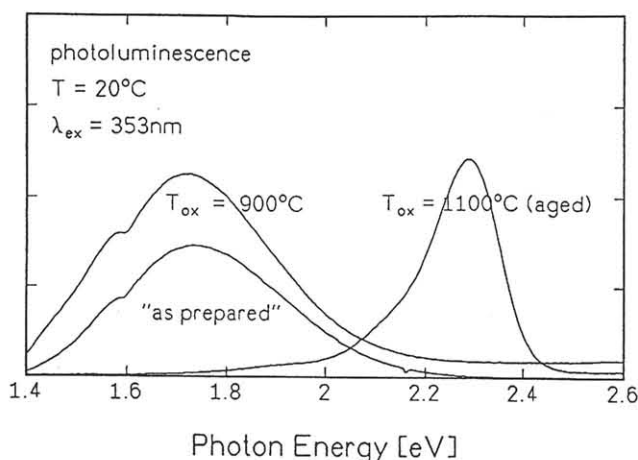


Fig.4 Luminescence spectra for the porous Si "as prepared", after oxidation at 900°C and for the high temperature 1100°C (aged) material.

luminescence is narrow and has a fast response time of ~ 4 nsec. By comparison, the red luminescence has a wide distribution of times ranging from 10^{-7} - 10^{-3} sec.

MECHANISM OF LIGHT-EMISSION

There is considerable speculation in the literature on the origin of the light in PS. The present work helps to clarify some points. It is unlikely to be the emission from either the siloxene /6/ or polysilane /7/. The luminescence is present in the fully hydrided and fully oxidized material. There are also problems with the quantum-well picture of the emission as proposed in /2,8/.

We propose a model in which the small Si particles, with surfaces alloyed with H or O, have a size-dependent shift of the absorption edge to higher energy. The excitation of electrons and holes takes place in the particles with large effective bandgap /9/. On the surface of the crystallites there are electronic states with lower energies. These originate from disorder in the surface Si-bonds as seen in the IR spectra. We postulate that the excited electrons and holes will relax on such a surface sites. When

both the hole and the electron recombine at the same site, the radiated photon will have an energy based on the local chemistry.

CONCLUSIONS

The oxidized material has proved to be more stable for storage at ambient conditions. It is less sensitive to irradiation with UV and keV electrons in cathodoluminescence /10/. In this sense we consider the oxidized PS, a superior luminescent material. It remains to identify the mechanism for the unusual green emission.

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