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FTIRS study of porous silicon at different oxidation stages

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Electroluminiscence (EL) in liquid of porous silicon (PS) has been attributed to radiative recombination of electrochemically generated holes from the bulk of the semiconductor and electrons injected into the conduction band of PS by species adsorbed on the surface. An examination of the surface of PS submitted to oxidation by means of Fourier Transform Infrared Spectroscopy indicates that the concentration of Si-H_x bonds does not significantly vary during the time interval in which EL is recorded, and therefore that the electrons belonging to the Si-H bonds do not intervene in the generation of EL. © *1999 Kluwer Academic Publishers*

1. Introduction

Porous silicon (PS) is currently being considered as a material for Si-based optoelectronics devices [1–3]. However, the extreme reactivity and fragility of PS samples limit their processing by conventional silicon integration technologies. Recently, it has been shown that partial oxidation of PS enhances its thermal and chemical stability [4]. It seems that the concentration of undesirable surface states in the interface between PS and oxidized PS is very low, so that they scarcely contribute to quenching of light emission.

Liquid-phase electroluminescence (EL) in PS has been attributed to radiative recombination of electrochemically generated holes in the bulk of the semiconductor and electrons injected into the conduction band (CB) of PS by species adsorbed at the surface or forming part of the electrolyte. The origin of this electronic injection is still under discussion. Some works attribute it to oxidation of Si-H bonds in the hydrogen rich passivation layer formed at the PS surface [5, 6]. In other studies [7, 8] some evidence have been put forward according to which an intermediate formed during the anodic galvanostatic experiment could be responsible for the necessary electron injection leading to EL emission. Such an interpretation is reinforced by the results obtained in this study, which show that the FTIRS band corresponding to Si-H_x does not significantly change in these samples before and after EL emission.

2. Experimental

PS were obtained from anodization of boron-doped (p-type) silicon wafers of (100) orientation, a thickness of 350 μm, and a resistivity of 0.1–0.5 Ω cm. The electrolyte for anodization consisted of a 2 : 1 HF (48 wt %)/ethanol (98%) mixture. The Si samples were etched galvanostatically at a current density of 50 mA cm^{-2} for 1–5 minutes under illumination in a specifically designed electrolytic cell [9]. After formation, the PS samples were rinsed with ethanol and immersed in a 0.1 M Na_2SO_4 aqueous solution. Anodic oxidation of the PS was then carried out under constant current density (50 mA cm^{-2}). A mercurous sulphate reference electrode (MSE) and a Pt gauze counterelectrode were used. The PS samples remained wet during the transit of solutions to prevent superficial cracking [10]. During the oxidation process, EL emission was observed and its integrated intensity recorded.

Electrochemical measurements were made with a computer driven PAR Mo. 273 electrochemistry system. EL measurements were acquired with an Aminco-Bowman Series 2 Luminescence Computer-controlled Spectrometer. The Fourier Transform Infrared Spectroscopy (FTIRS) analysis of the surface of the PS samples was performed at different oxidation stages with a Bruker 66 V spectrometer. It was equipped with an special accessory mod. Harrys Praying Mantis, in order to measure diffuse reflectance.

3. Results and discussion

Fig. 1 shows the chronopotentiogram resulting from the application of a constant current step to a PS sample. Between 0 and around 30 s a continuous oxidation of the PS surface is taking place. In order to make a more systematic study, the whole time interval has been divided in four ranges along which a change of the EL properties of the samples can be observed: R1 (0–7 s), in which PS is being oxidized, but EL is not observed; R2 (7–17 s), where EL is observed; R3 (17–25 s), in

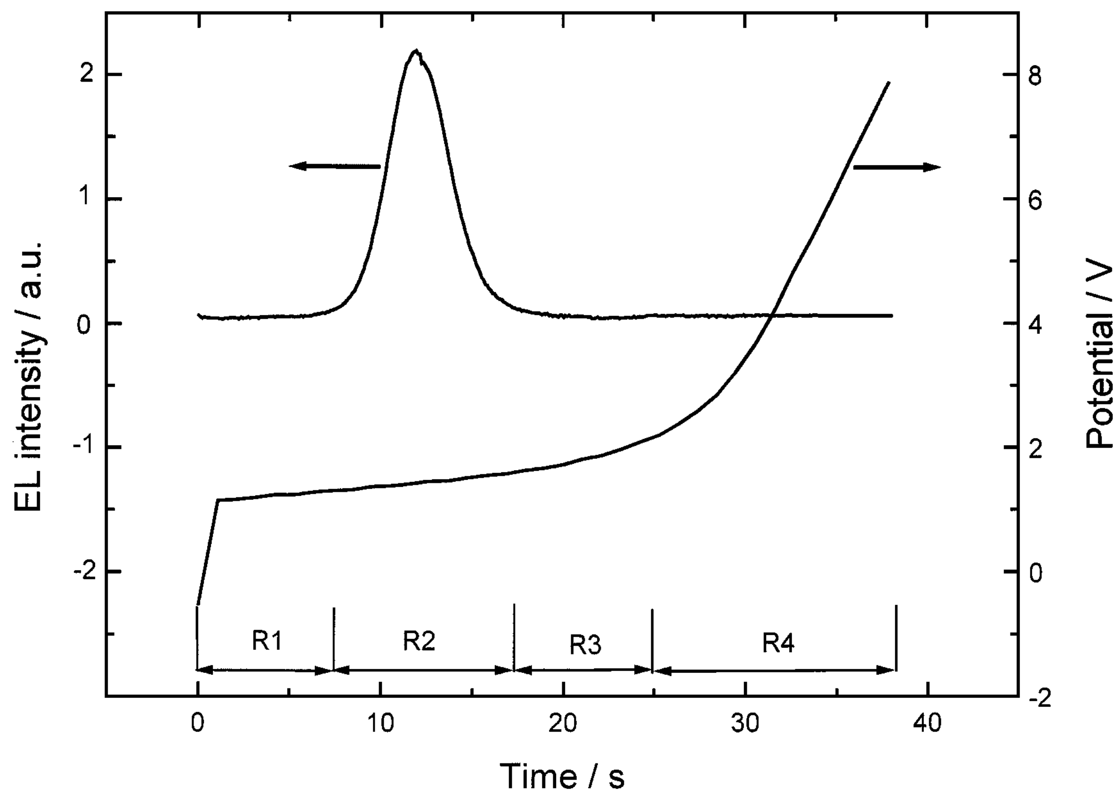

Figure 1 Chronopotentiogram recorded after the application of a galvanostatic step ($I = 6$ mA) to PS immersed in a Na_2SO_4 solution (25 °C) and Intensity (in arbitrary units) of the electroluminescence emitted during the galvanostatic step as a function of time. R1, R2, R3 and R4 correspond to the time intervals discussed in the text.

which the oxidation time is sufficiently long, so that EL is not further observed, although the potential has not yet started to increase significantly; R4 (25–40 s), time range at which a rapid increase of potential with time is observed.

In the galvanostatic oxidation of PS during R1, holes are injected by the galvanostat in the valence band (VB) of Si belonging to macrostructures with characteristics of bulk Si [11]. Thus, their recombination with electrons injected in the CB leads to light emission of ca. 1.1 eV, i.e., corresponding to the near-IR, where the detector employed is not sensible. Those holes which do not intervene in the emission take part in the oxidation of silicon surface sites to SiO_2 located in the bulk Si. Once this process is completed, Si surfaces sites corresponding to bulk Si disappear, so that the current externally imposed must be sustained by extraction of electrons from the VB located at more positive values, corresponding to smaller Si structures where quantum size effects are involved. Along R2, the combination of these holes and electrons injected in the CB gives rise to the emission of higher energy photons corresponding to the visible spectrum, i.e., to EL. In addition to EL emission, the surface of the porous structure is oxidized to SiO_2, so that when R3 is reached, most of the radiative recombination centers have been already oxidized [12] and, consequently, no EL emission can be detected. Once the process of oxidation of bulk silicon and thinner structures is completed, the potential rapidly increases (R4), originating a superficial cracking of the sample that gives rise to an increase of the number of non-radiative recombination centers.

FTIRS measurements have been performed on the samples to identify species present at the PS surface during the oxidation process. The FTIR spectra recorded give information about changes in chemical composition of the PS surface. These spectra show different bands which have been assigned to the presence at the silicon surface of Si-O and Si-H bonds (bands located at 1065–1130, and 2100 cm^{-1}, respectively [13]). Thus, FTIR spectra were recorded after reaching each of the four time intervals during which the PS samples are oxidized.

Fig. 2 shows the evolution of the characteristic bands attributed to Si-O_x and Si-H_x bonds as a function of the oxidation stage. Whereas the fresh, not anodized, PS samples do not give rise to any trace of oxide band (spectrum for R1 in the 1200–1000 cm^{-1} range), this band is always present whenever the PS sample is submitted to an electro-oxidation process (spectra recorded for PS samples whose oxidation was stopped after reaching R2, R3 and R4).

The spectra recorded between 1200 and 1000 cm^{-1} indicate that the concentration of surface oxide grows with the oxidation time (see bands for R2 to R4 in Fig. 2). Furthermore, the bands in the FTIR spectra widen with oxidation time, which indicates that different oxide types are being formed. Advanced oxidation stages are characterized by a shifted and less intense absorption band, reflecting that the sample becomes more amorphous. On the other hand, the FTIRS bands assigned to Si-H_x bonds (2050–2150 cm^{-1}) are not modified when the samples are examined after an oxidation time comprised within the time range at which EL is emitted. Thus, it can be concluded that the Si-H_x bonds do not disappear for samples oxidized until the end of R2, which exclude the oxidation of Si-H_x bonds as electron source for the EL emission. Fig. 2 for R3 and

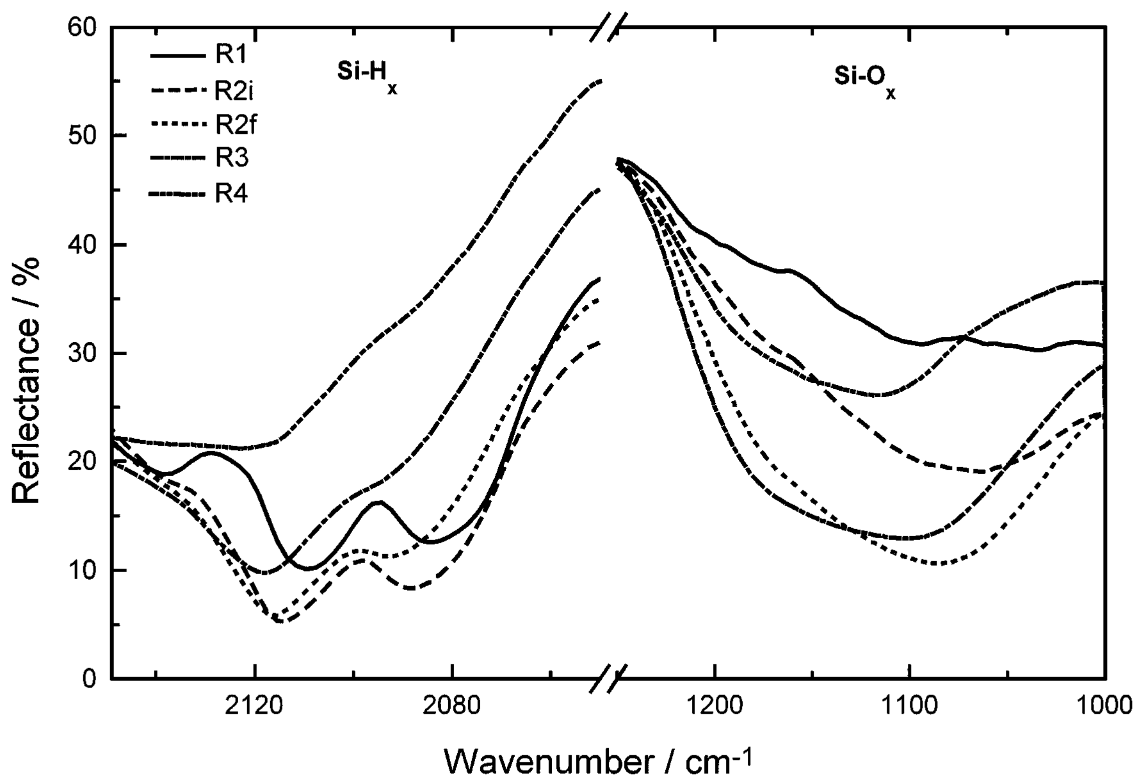

Figure 2 Infrared spectra of Si-O_x and Si-H_x bonds of PS samples at different oxidation stages correspond to the time intervals of Fig. 1.

R4 between 2050 and 2150 cm^{-1} shows that the band structure for SiH_x disappears and is substituted by a wide absorption band centered at ca. 2150 cm^{-1}.

In conclusion, the FTIR spectra recorded at different oxidation times of PS samples definitively exclude Si-H_x bonds as electron source for the EL emission process. This fact indirectly supports the idea that a substance formed as intermediate in the electrolyte by an oxidation process competing with light emission and SiO_2 formation, should be the source for electron injection in the CB of PS to give rise to EL.

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