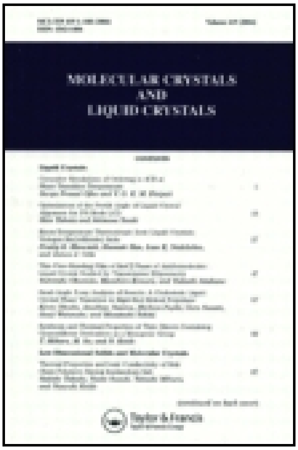

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Investigation of the Oxidation Effect of Porous Silicon During Electroluminescence by In Situ FTIR

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In situ FTIR spectra of porous silicon are measured during electroluminescence (EL). It was found that oxidation process of porous silicon surface occurs during EL, which is the main reason of the EL intensity decrease and red shift of peak energy with time.

Keywords: porous silicon; in situ FTIR; electraluminescence

INTRODUCTION

Porous Silicon (PS), which emits visible light, is currently an active field of research. The electroluminescence (EL) of porous silicon in electrolyte solution has been reported by several groups[1,2]. In addition to the potential applications this electroluminescence is very useful for the understanding of the charge injection mechanism governing the emission. Bysies et al. [3] reported the voltage-controlled EL by cathodically biasing in sulphuric acid containing sodium persulphate. The peak of EL spectra shifts toward shorter wavelengths with the increase in cathodic bias. In the previous work[4] , we found that the decrease of EL intensity was accompanied by a red shift of the EL peak at constant voltage with the elapse of time. In this letter, in situ FTIR is employed to investigate the surface structural change of porous silicon during electroluminescence. The relationship between EL behavior and changes of surface species was explored.

EXPERIMENTAL

Porous silicon layer was formed by electrochemical etching of lightly doped n-type (100) oriented silicon substrate. During the anodization process, the current density was kept constant at $5mA/cm^2$ for 10 min, and the Si wafer surface was illuminated with a 50 W halogen lamp. After formation, the porous silicon samples were immediately transferred into a quartz cell. A platinum wire plate served as a counter electrode and Ag/AgCl electrode was used as reference electrode. The EL of porous silicon was obtained in a freshly prepared 1M H_2SO_4 aqueous solution containing 0.2M $(NH_4)_2S_2O_8$ and a small quantity of ethanol. The emitted EL spectra were recorded on a Perkin-Elmer LS 50B luminescence spectrometer.

In situ FTIR experiments were carried out using a Nicolet 730 FTIR single-beam apparatus equipped with a liquid-nitrogen cooled MCT-B detector. The spectroelectrochemical cell has been described in ref. 5. The electrolyte was an aqueous solution containing 0.2M $Na_2S_2O_8$ and 0.15 M Na_2SO_4. The in situ FTIR experiments were performed at two potentials, reference potential E_1 and sample potential E_2. The sample spectrum is obtained by plotting $\triangle R/R$ vs. wavenumbers, where $\triangle R/R = [R(E_1)-R(E_2)]/R(E_2)$, with $R(E_1)$ or $R(E_2)$ as the single beam spectrum recorded at potential E_1 or E_2, respectively. In the resulting spectra, the positive going band indicates that more IR energy is absorbed at E_1 than at E_2; the negative going band corresponds to a greater IR absorbed at E_2 than at E_1.

RESULTS AND DISCUSSION

Fig.1 shows the evolution of EL spectra as a function of time at -2.5V vs. Ag/AgCl. It is seen that the EL intensity decreases gradually with time while the peak energy of EL shows red shift.

Fig.2 displays the in situ time resolved IR spectra obtained at reference potential of -0.3 V and sample potential of -2.5V (vs. SCE). The time interval between successive spectra was 178 seconds. The spectra show the following features. There is a positive going band near 2106 cm^{-1} and a negative going band near 2246 cm^{-1}, whose intensities increase remarkably with the reaction time, respectively. Another negative going band at 1060 cm^{-1} increases progressively in intensity.

The absorption peak at 2106 cm^{-1} was assigned to Si-H_2 stretching mode[6]. The higher frequency absorption at 2246 cm^{-1} is attributed to Si-H stretch from a Si atom which is back-bonded to oxygen atoms, i.e. O_3-Si-H[7].

The intensity increases of both positive going band at 2106 cm^{-1} and negative going band at 2246 cm^{-1} suggests that the SiH_2 consume and O_3SiH generate on the surface of porous silicon during the EL process. The blue shift of Si-H absorption frequency with time reflects partial oxidation of porous silicon surface. The absorption intensity at 1060 cm^{-1} corresponds to the Si-O-Si stretch mode in amorphous SiO_2 [8], which also supports the mechanism that the surface oxidation occurs during the EL.

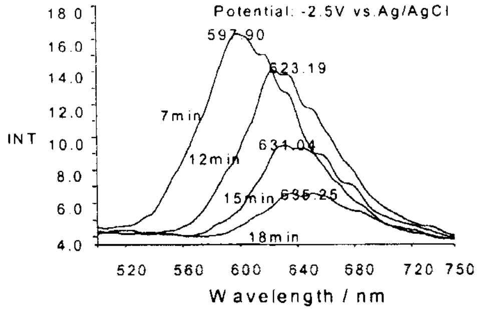

Fig. 1 Time dependence of EL spectra of PS under cathodic polarization Time dependence of EL spectra was investigated at a constant voltage.

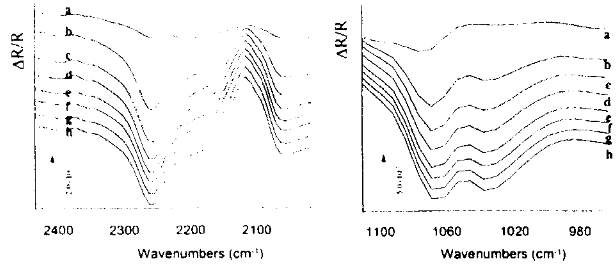

Fig. 2 *In-situ* time resolved IR spectra of PS at -0.3V and sample potential at -2.5V(*vs.*SCE) in 0.2M $Na_2S_2O_8$ solution.a: 89s; b:267s; c:445s; d:623s; e:801s; f:979s; g:1157s; h:1335s

The possible explanation is as follow. Because of the huge surface area, porous silicon has a strong reactivity. Lots of bubbles can be seen when a porous silicon is dipped into solution under open circuit. At cathodic polarization, persulphate is reduced in two discrete steps on many semiconductor interfaces[9]. First the $S_2O_8^{2-}$ is reduced to a very reactive intermediate oxidant $SO_4^{-\cdot}$ by capturing electron from conduction band of porous silicon. Second the $SO_4^{-\cdot}$ injects a hole into the valence band of porous silicon. The injected hole can recombine with an electron from the conduction band to give visible light emission.

When the potential is more negative than -1.3V, the H^+ ion reduction takes place by an electron exchange with the conduction band. It was observed clearly that a large number of bubbles escape quickly from porous silicon electrode. Obviously this reaction will compete with the reduction of $S_2O_8^{2-}$. The electron of conduction band hence is consumed by both $S_2O_8^{2-}$ and H^+ ions. If the injected holes are not combined with electrons on conduction band immediately, the oxidation of porous silicon will occur consequently. Considering the fact that the Si-Si bond energy is smaller than Si-H energy (176 and 295 kJ. mol^{-1}, respectively), the Si-Si bond will be broken firstly. O atom insertion into the Si-Si back-bonds results in O_xSiH surface species, which is evidenced by the increase of absorption intensity at 2246 cm^{-1} with reaction time.

Surface oxidation leads to the increase of resistivity of porous layer. At a given potential, the current flow is hindered. This occurs at first in the smaller crystallites which results in a red shift of EL spectra because of quantum size effect. The oxidized layer continuously increases with the increase of polarization time which leads to the decrease of EL intensity and complete eliminating of EL at end.

Acknowledgements

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