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Comparison of Blue Luminescence Between Spark-processed Photoluminescing Silicon and Ambient Air Aged Anodically Etched Porous Silicon

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Ambient air aged anodically etched porous silicon (PS) and spark-processed silicon (sp-Si) show interesting similarities and dissimilarities in some of their luminescence-related properties. Among these similarities are: (1) the photoluminescence (PL) peak maximum in the blue/violet (410 nm); (2) the blue/violet PL peak positions are essentially unchanged with temperature ; (3) PL decay times in the nanosecond region which are independent of the detection wavelength, which is much faster in decay times compared to that of observed decay time in SiO_2. Among the dissimilarities are: (1) the PL intensity of blue/violet luminescence, namely, the PL intensity of sp-Si is at least 2 orders of magnitude larger than that of an ambient air aged PS; (2) the blue/violet PL intensity of sp-Si is more stable than that of ambient air aged PS under UV illuminations; (3) FTIR spectra of sp-Si favor those modes, which involve silicon -oxygen bonds in SiO_2 stoichiometry, whereas ambient air aged PS can be considered as a nonstoichiometric oxide judging from the observed vibrational spectra.

Key words : Photoluminescence, Blue luminescence, Porous silicon, Decay time

I. Introduction

Silicon is one of the most widely investigated material and, in its crystalline form, has been the basic material in microelectronics. The utilization of silicon for optoelectronic devices compatible with existing silicon technology has been an important challenge during the last decade. However, crystalline silicon only displays weak emission in the near infrared at energies below the energy gap (Eg~1.1 eV) due to its indirect bandgap. Therefore, the development of silicon as an optically active devices has been limited. The situation is changed in the 1990's with the discovery of visible photoluminescence (PL) at room temperature.[1,2]

Porous silicon which is obtained by electrochemical etching has attracted a large number of investigation not only to PL but further to its application as an optoelectronic devices. A large surface area of porous silicon renders a difficulty of delineating the mechanisms of the strong PL from PS.

Anodic etching of silicon leads to an high efficiency room temperature PL usually in the orange-red part of the visible spectrum. Using a post treatment of light emitting PS in purified boiling water, blue green luminescence can be observed, even though this method shows somewhat lack of reproducibility.[3] The blue luminescence of PS also emerges after rapid thermal oxidation above 800°C[4,5] and atmospheric aging of thin PS.[6] Spark processed Si (sp-Si) also luminesces in the blue and the green spectral region.[7-9] Interestingly, the blue PL can be detected when the PS contains a large amount of oxygen. Spark processed silicon as well as ambient air aged PS have been observed, mainly in the aspect of above mentioned room temperature PL in the blue spectral region and the involvement of oxidized layers in one way or another. Current studies of the blue PL attribute their origin to the silicon crystallites,[10] Si quantum wires,[11] silanol groups adsorbed in a SiO_2 network,[12] a SiO_2 and oxide related species.[9]

There exist a number of significant differences between ambient air aged PS and sp-Si, thus the purpose of this paper is to delineate the difference between aged PS and sp-Si.

II. Experimental Procedure

The porous silicon samples were prepared by electrochemical etching of Boron doped (100) p-Si (8~12 Ωcm). Anodization was conducted for 10 min under constant current density of 1 mA/cm^2 with concomitant UV light illumination in 1:9 HF:ethanol solution. Then, porous silicon samples were ambient air aged for 1 month. On the other hand, spark processing was employed to fabricate blue and green luminescing Si. The sample preparation involved a high frequency (kHz range), high voltage (several thousand volts), and low current density (several mA) electric sparks between a silicon substrate and a counter electrode, which was a

tungsten tip. Generally, sample preparation was conducted by applying unipolar current pulses between 1 mm spark gap. The repetition frequency was chosen to be 16.7 kHz which led to a pulse length of about 0.02 μs repeated every 60 μs.[7]

Two types of spark processed Si samples were produced. First, a stream of dry air was directed during the spark processing toward the front surface of Si wafer. This technique yielded the strong blue/violet (410 nm=3 eV) photoluminescing substance. A less intense green PL (525 nm=2.36 eV) was obtained from Si which was spark processed at ambient air conditions

Photoluminescence measurements were performed by a conventional setup with voltage measurement technique or photon counting mode. Optical excitation was achieved by a pair of lenses after passing a long pass band filter which blocks scattered laser light. The cut on wavelength of this filter (50% transmission) was 348 nm. The photoluminescence dynamics were performed either in a system using 390 nm pulsed beam which was produced by the second harmonic generation of a mode-locked Al_2O_3 : Ti laser pumped by an Ar^+ laser or using an excitation wavelength of 300 nm provided by the second harmonic of a mode-locked dye laser. The pulse duration and instrumental resolution were 1.7 ps and 20 ps for the former, and 2~3 ps and 100 ps for the latter, respectively.

Fourier transform infrared (FTIR) spectra were used to investigate the Si-O vibrational mode of the ambient aged PS, sp-Si, and other relevant materials such as Si-O compound.

III. Results and Discussions

Typical PL spectra, which are collected both at room temperature (depicted as solid line) and 77 K (depicted as dotted line), which display blue and green luminescence are depicted in Fig. 1 The laser power density was 0.3 W/cm^2. Both air-blown sp-Si and ambient air aged porous silicon samples display the PL maximum near 410 nm (Fig. 1 curves a and c), whereas strongly oxidized porous silicon exhibit the PL centered near 460 nm.[4] In contrast to this, ambient air sp-Si has a PL maximum near 525 nm, which is in the green spectral region (Fig. 1 curve b), and decreases the PL intensity by one order of magnitude compared to that of air-cooled sp-Si. The intensity of blue/violet luminescence from ambient air aged PS is at least 2 orders of magnitude smaller than that for the air-blown sp-Si The PL spectra measured at 77 K exhibit different temperature behavior. Specifically, the PL peak maximum (Fig. 1 curve b) from ambient air sp-Si shows the red shift at 77 K, whereas the blue/violet luminescence band from both the air-cooled sp-Si (Fig 1 curve a) and the ambient air aged PS (Fig. 1 curve c) remains nearly the same between room temperature and 77 K. It is interesting to

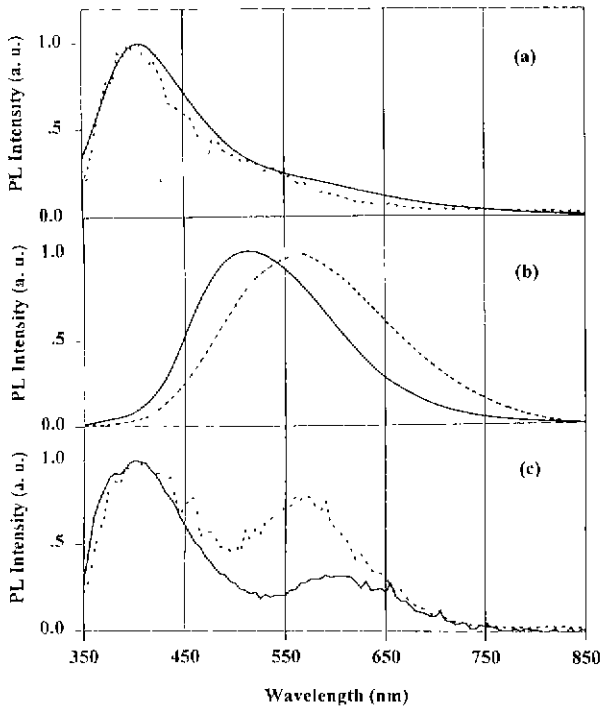

Fig. 1. Room temperature PL spectra (depicted as solid line) and 77 K PL spectra (depicted as dotted line) of (a) blue/violet luminescing sp-Si (b) green luminescing sp-Si, and (c) blue/violet luminescing ambient air aged PS, excited by the 325 nm line of CW He-Cd laser.

note the two PL band structure, i e. blue/violet and red PL from ambient air aged porous silicon. The blue/violet PL band (curve c) does not show any shift at 77 K as already mentioned, whereas the red PL band is blue shifted to of about 570 nm and yellow emission can be clearly observed during the measurements. We could not observe the blue/violet PL shift to a higher energies with decreasing temperature, as is the case with the bandgap energy of crystalline or amorphous Si. Since free exciton transitions (such as in Si nanocrystallites) are expected to follow the bandgap change with temperature, one can conclude that the blue/violet luminescence is unlikely to be correlated with that type of transition. In contrast to the blue/violet PL band, the red PL band from ambient air aged PS shows the expected increase of bandgap with decreasing temperature.

Figure 2 shows the decrease in the PL peak intensity as a function of time after the blue and green photoluminescing samples have been exposed to 325 nm He-Cd UV laser radiation, applying a laser power density of 0.3 W/cm^2. It is observed in the given time interval PL intensity of sp-Si prepared in air (curve (a)) essentially remains stable, whereas PL intensity of ambient air aged PS (curve (b)) decreases rapidly than that of sp-Si, but with improved stability than that of the red PL from PS (curve (c)). The rapid degradation of PS was shown to be correlated with hydrogen loss due to high energy illumination (threshold near 3 eV)[10] or with the release of

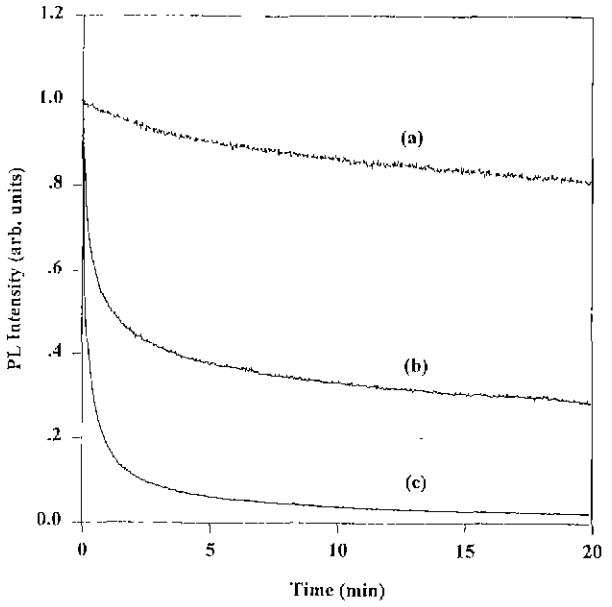

Fig. 2. Decrease of PL intensity as a function of exposure time to 325 nm laser light (0.3 W/cm^2). (a) blue/violet luminescing sp-Si (b) blue/violet luminescing ambient air aged PS, and (c) red luminescing anodically etched PS.

SiH_3 due to heating effects.[14] Thus, the observed stability of blue/violet luminescence from sp-Si and improved stability of ambient air aged PS compared to freshly prepared PS can be explained by the formation of oxidized layer which suppresses nonradiative recombination (see below).

The luminescence decay curves which are measured at various wavelengths are depicted in Fig. 3. In all cases the PL decay does not depend significantly on the emission wavelengths. The decay dynamics is non exponential and the curves cannot be fitted by a bimolecular recombination law nor by a stretched exponential function. Specifically, an initially fast decay with a time constants of about 2 ns is superimposed by a much slower decaying tail with time constants of about 10-30 ns for sp-Si. However, ambient air aged PS (Fig. 3 curve c) displays much faster decay time of subnanosecond in contrast to those of sp-Si. The observed decay time constants of sp-Si are substantially shorter than the lifetimes of red luminescing PS (typically 1~10 μs at room temperature).[15] However, an analogous fast PL decay in the range of 10 ns has been reported for the blue-green band of strongly oxidized PS.[4,16] The PL bands of SiO_2, which fall in the same wavelength range, also display much slower in their decay characteristics. For the 1.9, 2.2, 2.7 and 3.1 eV transitions in silicon oxide, the decay time constants of 12-14 μsec, 60~80 nsec, 9.4~10 ms, and 110 μs were measured, respectively.[17-20] Thus, it seems unreasonable to consider transitions as they appear in SiO_2 as the possible candidates to explain the observed blue/violet and green PL.

Of particular interest is a comparison between the in-

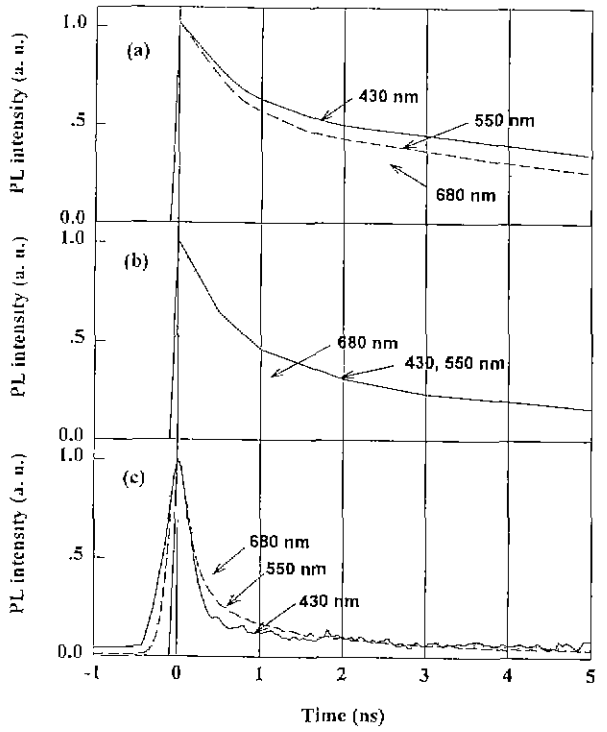

Fig. 3. PL decays for (a) blue/violet luminescing sp-Si (b) green luminescing sp-Si, and (c) blue/violet luminescing aged PS at several wavelength.

frared vibrational spectra of sp-Si and ambient air aged PS samples. The detailed Fourier transform infrared (FTIR) spectra of sp-Si have been amply described in the literature.[21] It should be mentioned in brief that the hydrogen-involved vibrational modes connected with Si are clearly missing for sp-Si in contrast to freshly anodically etched PS and siloxene. The amount of stoichiometry in SiO_2 or non-stoichiometry in SiO_x for the blue/violet luminescing Si samples can be inferred by inspecting the Si-O stretching vibrations between 1050 and 1170 cm^{-1}. Figure 4 depicts a comparison of vibrational modes from fused SiO_2, sp-Si (prepared under air flow and stagnant conditions), ambient air aged PS, vapor deposition of SiO and Si in the range between 800 and 1400 cm^{-1}. It is evident that the spark-processed specimens are in close resemblance to the general absorption curve of fused SiO_2. Specifically, sp-Si displays a vibrational mode near to 1120 cm^{-1} with a shoulder at 1250 cm^{-1} which stands for asymmetric Si-O-Si stretchings and which are both characteristic in stoichiometric SiO_2. In contrast, the absorption modes for ambient air aged porous silicon (curve (d) in Fig. 4), vapor deposited SiO (curve (e) in Fig. 4) and for Si with implanted O (curve (f) in Fig. 4) are shifted or showed no particular features, respectively. Therefore, the ambient air aged porous silicon can be inferred as a nonstoichiometric. The alternate Auger electron spectroscopy (AES) analysis also shows the nonstoichiometry of oxide (not shown). Thus, the improved stability of blue/ violet luminescence from sp-Si com-

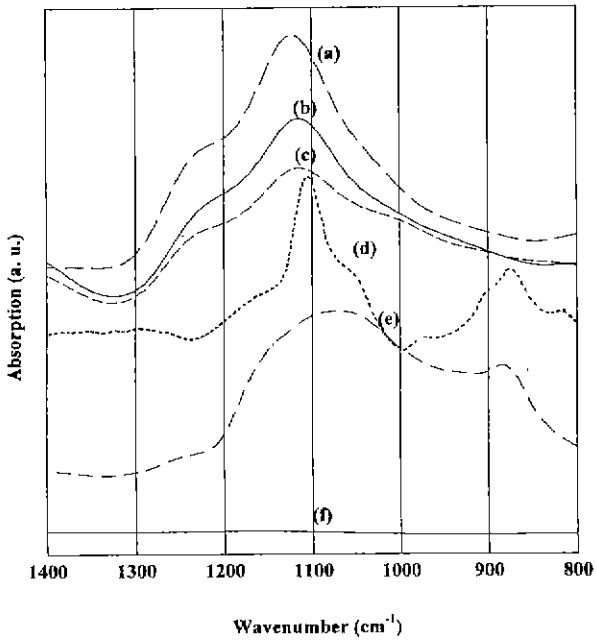

Fig. 4. Absorption Fourier Transform infrared (FTIR) spectra of (a) fused SiO_2, (b) blue/violte luminescing sp-Si, (c) green luminescing sp-Si, (d) ambient air aged PS, (e) vapor deposited SiO on Si, and (e) Si implanted by O (25 KeV, 2×10^{16} cm^{-2}).

pared to ambient air aged PS can be explained by the stable stoichiometric oxide passivation which suppresses the nonradiative recombination. From the fact that the blue/violet PL does not show any temperature behavior as depicted in Fig. 1 and displays fast PL decay time constants (Fig. 3), it is more reasonable to consider localized state with radiative transitions as the possible candidate of the blue/violet PL.

IV. Summary

Both ambient air aged PS and sp-Si display similar properties such as blue/violet PL near 410 nm, and show no PL peak shift at 77 K and exhibit fast PL decay times below ns and independent of wavelength. The PL intensity of sp- Si is at least 2 orders of magnitude lager than that of ambient air aged PS. However, the thickness of ambient air aged PS is at least 2 orders of magnitude smaller than that of sp-Si ,i.e. much small in luminescence active volume. Thus, the overall PL intensity might be in the same order of magnitude, if one consider the same luminescence active volume. The sp-Si possesses better PL stability under UV exposure than ambient air aged PS. This behavior can be explained by the fact that sp-Si were passivated by stable stoichiometric oxide i.e. SiO_2. In contrast to this, the surface of the ambient aged thin PS layer were passivated by less stable nonstoichiometric oxide as determined by vibrational spectra.

Acknowledgments

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