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X-ray emission spectra and the effect of oxidation on the local structure of porous and spark-processed silicon

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Abstract. The paper presents a comparison of Si $L_{2,3}$ x-ray emission spectra of *porous* silicon (P-Si) and of *spark-processed* silicon (sp-Si). Both types of Si structure display strong photoluminescence in the visible range of the spectrum. Porous samples were prepared by anodization of n^- and p^+ Si wafers. Whereas for the P-Si processed from p^+ Si the presence of some amorphous silicon is detected, the x-ray emission spectra of porous Si prepared from n^- Si display a higher content of SiO_2. For spark-processed Si the Si $L_{2,3}$ x-ray emission spectra reveal a much stronger degree of oxidation which extends to depths larger than 10 000 Å. Furthermore, the chemical state of silicon atoms of sp-Si measured at the centre of the processed area is close to that of silicon dioxide, and depends slightly on the emission maximum. Specifically, green-photoluminescing sp-Si shows a higher degree of oxidation than the blue-luminescing specimen. However, the depth of oxidation consistently decreases for areas with weak photoluminescence and without photoluminescence. Possible origins for the photoluminescence are discussed.

1. Introduction

Porous silicon (P-Si) has been studied for quite some time because of its usefulness as a microelectronic material. Particular interest arose after the discovery that it strongly photoluminesces in the visible spectral range [1]. A review of papers devoted to P-Si is given in reference [2]. Photoluminescence (PL) spectra of P-Si contain peaks in the red and under certain circumstances also in the green–blue range. The PL is occasionally explained as being the result of quantum confinement effects of charge carriers in Si crystals which are limited in size (formed during the preparation of P-Si) [1], or as being caused by luminescence of different chemical species (Si, O, H) on the surface of P-Si [3–6], or by disorder in the system [7]. The former explanation is probably valid mainly for the red part of the PL spectrum. The latter appears to describe PL in the green–blue part of the spectrum.

Spark-processing of silicon (sp-Si) has likewise been shown to yield a strong room temperature PL and cathodoluminescence [8, 9]. This strong PL, according to reference [9], cannot be attributed to the silicon oxide matrix nor to impurities in the matrix. It

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was found that the PL peak position of sp-Si depends on the preparation conditions and is different for processing in *stagnant* compared to in *flowing* air [10].

For a better understanding of the origins of photoluminescence of P-Si and sp-Si it might be useful to study the local structure of the materials. So far, P-Si has been investigated by x-ray photoemission [11], x-ray absorption spectroscopy [12–15] and transmission electron microscopy [16]. Differences between Si L x-ray absorption spectra of *porous* and crystalline silicon were pointed out by van Buuren *et al* [14] and explained in terms of the inhomogeneous structure of P-Si. The absorption spectrum of P-Si in this case is approximated by the absorption spectrum of *crystalline* Si (c-Si) the energy of which has been adjusted to simulate an average quantum shift [14]. Si K x-ray absorption near-edge spectra (XANES) showed the presence of silicon–silicon disorder bonds [14] in bulk *porous* silicon and the existence of a comparable number of Si–O and Si–OH bonds [13]. A substantial similarity between the Si K- and Si L-edge x-ray absorption of P-Si and layered polysilane (Si_6H_6) has been found by Dahn *et al* [12].

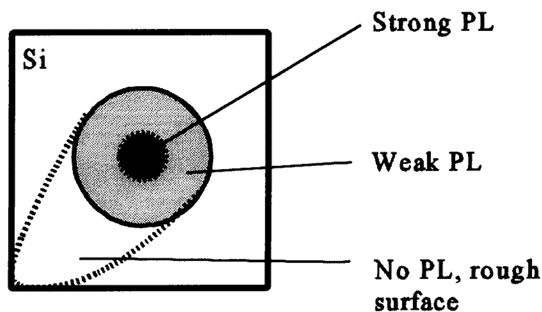

Figure 1. A schematic representation of *spark-processed* Si indicating areas having strong, weak, and no PL, respectively.

In short, the results pertaining to the structure of P-Si are contradictory. On the other hand, sp-Si has not yet been studied within the same context. Thus, the present paper reports on investigations of the local electronic structure of *porous* and *spark-processed* silicon utilizing x-ray emission spectroscopy. It has been shown that this technique is very sensitive to the chemical bonding and its modification under different sample treatments in Si-containing materials [17–19].

2. Experimental procedure

Two *porous* Si layers were prepared at the Institute of Scientific and Industrial Research of Osaka University. Sample P-Si(2) was prepared by anodic etching of an n^- Si(100) substrate at 80 mA cm^{-2} in a solution of hydrofluoric acid under white light exposure from a 300 W tungsten lamp for 0.5 min. The specimen was exposed to air for about two years prior to the measurements described here. Sample P-Si(1) was prepared by anodizing p^+ Si at 20 mA cm^{-2} for 5 min in darkness. This sample was manufactured six months before measuring the XE spectra. For both samples, the thickness of the porous layer ranged between 3 and 5 μm. The preparation details as well as the optical properties of these samples were already reported in reference [11]. For comparison, bulk single crystals of Si, SiO_2 and a thin film of amorphous Si (a-Si) were included for this investigation.

Spark-processed Si was prepared in the Department of Materials Science and Engineering of the University of Florida. This was accomplished by utilizing unipolar high-voltage ($\sim$15 kV) direct-current pulses which were applied between a tungsten tip (the

anode) and a silicon wafer (the cathode). This process builds up a circular area of 1 to 5 mm in diameter in which the strongest PL is found at wavelengths between 400 and 600 nm, depending on the conditions during preparation. The white–grey centre is surrounded by a halo-like, brownish structure. Both parts are characterized by small holes of about 10 μm in diameter. The thickness of the sp layer extends up to 250 μm directly below the counter-electrode and tapers off toward the perimeter.

To elucidate the relationship between processing parameters, photoluminescence and structural properties of sp-Si, two different sets of conditions for sample preparation were chosen. One type of specimen, which has a strong PL in the UV/blue region ($\lambda_{max} = 415$ nm), was prepared by spark processing in flowing air. The surrounding, asymmetric layout of the spark-processed area (see figure 1) results from the air flow and displays no PL. Another type of sp-Si was processed under stagnant air conditions. The photoluminescence of this specimen peaks in the green region ($\lambda_{max} = 525$ nm).

PL measurements of sp-Si were performed at room temperature utilizing a single-grating monochromator equipped with a photomultiplier as the detector. For excitation a HeCd UV laser having a wavelength of 325 nm was used. To block scattered laser light a long-pass band filter (50% of transmittance at 348 nm) was positioned between the sample and the collection optics.

Si $L_{2,3}$ (2p $\rightarrow$ 3s3d transition) x-ray emission spectra (XES) were measured by using a small-spot x-ray emission spectrometer having a diffraction grating ($N = 600$ lines mm^{-1}, $R = 2$ m) and electron excitation [20]. The spatial resolution was 4–5 μm and the energy resolution was about 0.4 eV. The sample under investigation formed the target of the x-ray tube which was operated at 2–6 keV and 300 nA. The measurements of the Si $L_{2,3}$ XES of P-Si(1), P-Si(2), and of *spark-processed* Si prepared in *stagnant* air and in *flowing* air were performed at the Institute of Metal Physics (Yekaterinburg, Russia).

Si $L_{2,3}$ x-ray emission spectra (XES) correspond to radiative transitions between the valence states and the Si 2p core level which can be ionized by electron or photon excitation (in our experiments electron excitation was used). As a result of the dipole selection rules the Si $L_{2,3}$ XES probes the 3s + 3d partial density of states localized at the silicon atoms. It was shown in our previous publications [20–22] that the site-projected 3s + 3d density of states extracted from Si $L_{2,3}$ XES is very sensitive to the chemical bonding. At the energy resolution of about 0.4 eV (used in our experiment) the shapes and energetic positions of the spectral features are sufficiently different in the crystalline and amorphous states of pure Si to permit a study of the local structure of *porous* silicon with the help of Si $L_{2,3}$ XES.

The use of electron impact excitation for the Si $L_{2,3}$ XES at different accelerating voltages in the x-ray tube allows us to probe different layers of the target because of the pronounced dependence of the electron range and therefore of the depth of origin of the x-rays as a function of the electron excitation energy [23]. It has been shown that the use of both modes (high-energy resolution and depth-profiling analysis) provides in-depth profile estimations of different phases in Si-containing materials [17, 18]. Given this opportunity we analysed the local structure of *porous* and *spark-processed* silicon as functions of the depth.

3. Results and discussion

The x-ray emission Si $L_{2,3}$ spectra for P-Si(1), and P-Si(2) along with c-Si and SiO_2 measured at electron energies of 2, 4, and 6 keV are depicted in figures 2(a) and 2(b). It can be seen that the spectra for P-Si(1) prepared from p^+ Si are similar to those for c-Si (though it had been stored in air for six months). This effect is typical for the bulk of the

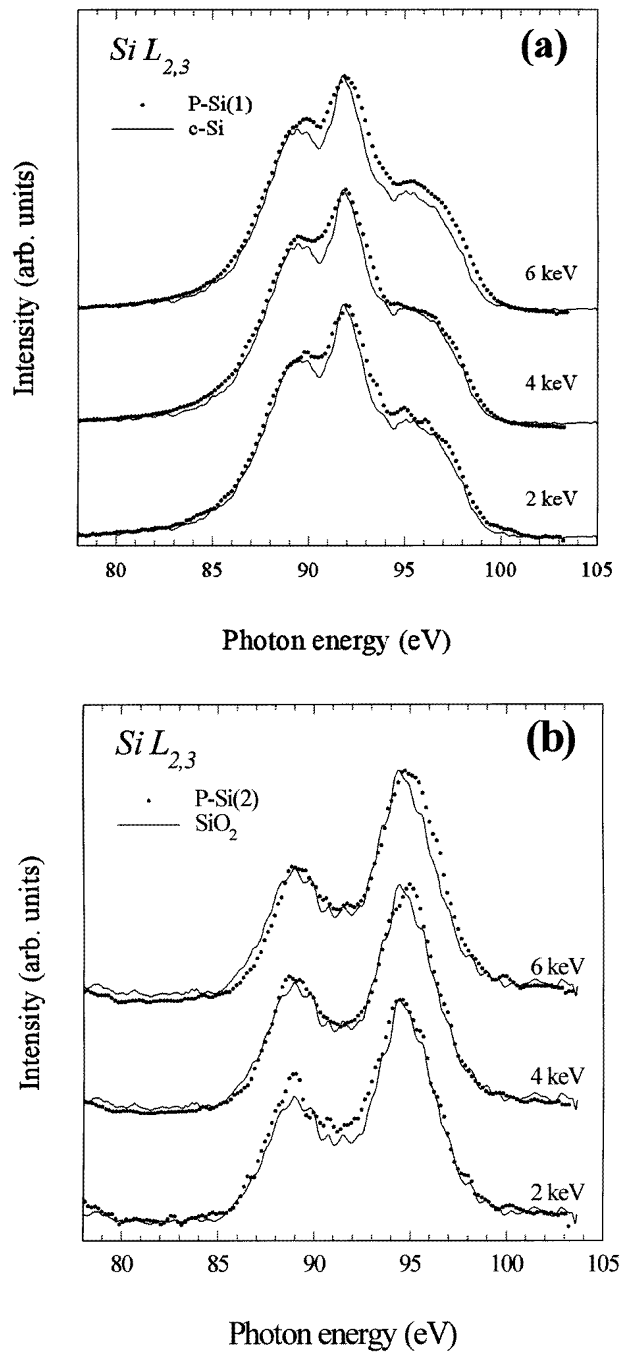

Figure 2. (a) Si $L_{2,3}$ x-ray emission spectra of P-Si(1) and c-Si measured using electron excitation energies of $E = 2$, 4 and 6 keV. (b) Si $L_{2,3}$ x-ray emission spectra of P-Si(2) and SiO_2 measured using electron excitation energies of $E = 2$, 4 and 6 keV.

sample as the spectra do not change for different accelerating voltages in the x-ray tube. In contrast to this result, Si $L_{2,3}$ XES for porous silicon (P-Si(2)) obtained from n^- Si and exposed to air for about two years (P-Si(2)) were found to be very close to those of SiO_2 (figure 2(b)).

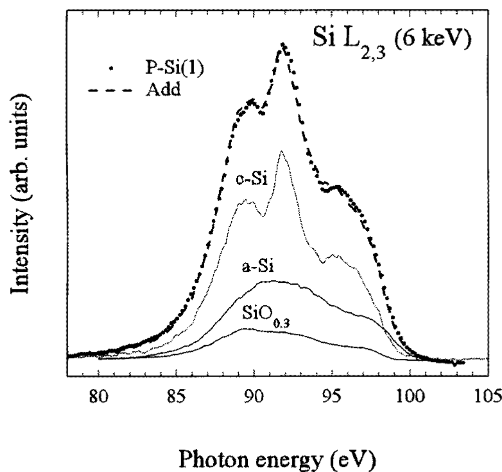

Figure 3. A superposition of the Si $L_{2,3}$ XES of c-Si, a-Si, and $SiO_{0.30}$ in the ratio 0.65:0.25:0.10 and their comparison with the spectrum of P-Si(1) measured at 6.0 keV.

It is necessary to point out that the intensity minimum between two spectral features for Si $L_{2,3}$ XES of P-Si(1) at photon energies of 89.3 and 92.0 eV is not as distinct as that for c-Si (see figure 2(a)). This smearing out can probably be attributed to the contribution of the Si $L_{2,3}$ XES spectrum of some a-Si or $SiO_{0.30}$ whose spectra have flat extended maxima in this energy range. To check this we have superimposed Si $L_{2,3}$ XES of c-Si on those of a-Si and $SiO_{0.30}$. As a result, we found that for the ratio 0.65:0.25:0.10 the additive spectra reproduce quite well the spectra of P-Si(1). However, other compositions for these components are also possible because of the similar shapes of XES spectra for a-Si and SiO_x (with $x < 0.5$). Figure 3 shows the superposition of the spectra in comparison with the spectrum of P-Si(1) measured at the electron energy of 6 keV. The spectrum of $SiO_{0.30}$ has been taken from the work of Wiech *et al* [24]. The contribution of a-Si to the forming of the spectra of P-Si(1) is prominent. We therefore conclude that the local structure of *porous* silicon prepared from p^+ Si can be characterized by short-range order which has features typical for crystalline and amorphous silicon. This conclusion is in accord with observations utilizing high-resolution transmission electron microscopy which show that P-Si consists of small branches and particles that are crystalline in the centre surrounded by an amorphous layer (see reference [25]).

X-ray emission spectroscopy utilizing some variation in energy of the incident electrons allows the analysis of different layers since the x-ray yield depth is a function of the electron excitation energy. In order to obtain information regarding the depth output of x-rays, we have calculated the simulation of the Si $L_{2,3}$ intensity distribution with depth for electron energies amounting to 2, 4, 6, 8, and 10 keV. The x-ray intensity $I(\rho z)$ generated by atoms at depth z was presented as the product of the electron distribution function $\omega(\rho z)$ with the absorption factor $\exp(-\mu_m \rho z/\cos\psi)$. Here, ρ is the material density, μ_m is a mass absorption coefficient, and ψ is the collection angle of x-rays with respect to the normal

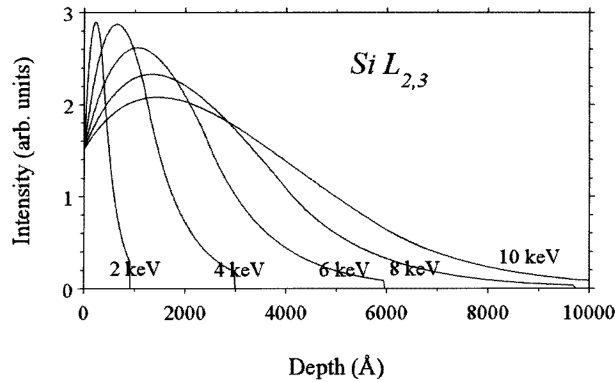

Figure 4. The dependence of calculated Si $L_{2,3}$ x-ray emission spectral intensities as functions of the depth in Si on the electron excitation energies.

to the sample surface. The electron distribution function $\omega(\rho z)$ was approximated by a parabola extending from ω_0 (at $\rho z = 0$) with the maximum at $\rho z = h$ and for $\rho z \gtrsim 1.5h$ by an exponent [26]. The maximal depth of the electron penetration (in Å) was calculated according to work by Feldman [23]:

$$(\rho z)_{max} = 250(E^n - E_c^n)A/Z^{n/2}.$$

Here, A and Z are the effective atomic mass and the atomic number of the target material, E and E_c are the energy of incident electrons and the ionization energy of the probed core level (keV), respectively, and

$$n = 1/(1 - 0.29 \log_{10} Z).$$

The method of calculation is more elaborately described in [18]. The results of the calculations are presented in figure 4. Hence, with the Si $L_{2,3}$ emission spectra excited by electrons having energies of up to 10 keV we can analyse layers as thick as 10 000 Å.

Thus, the results for P-Si(2) allow us to state that the oxidation of Si occurs at a depth of more than 10 000 Å (1 μm). The difference in the degree of oxidization when compared with P-Si(1) is probably due to the difference in substrate rather than to the period of time since preparation. Canham *et al* [27] have shown for *porous* Si, that oxygen atoms penetrate into the remaining structure by up to about 1.5 μm. Our results for P-Si(2) strongly support this conclusion. Moreover, we argue that we have found that SiO_2 is formed over the full range of depth which was probed.

The XE spectra taken on *spark-processed* silicon (sp-Si) for different areas of the specimen are presented in figures 5(a)–5(c). The spectra of the central area which displays strong PL (figure 5(a)) are very similar to that of SiO_2. They virtually do not change with the voltage on the x-ray tube. This probably means that *spark processing* induces some oxidation of Si which is homogeneous through the depth. The degree of oxidation of the Si atoms in this area is close to that for SiO_2, as can be concluded by comparing them with the spectra for SiO_x ($x = 0.3$–2.0) [24].

For the areas which display only weak or no PL we have observed some weakening of the oxidation with depth (see figures 5(b) and 5(c)). These changes of the spectral shape with electron energy are probably due to a SiO_2 layer on the surface. We estimated that the thickness of this layer is about 1000–1200 Å for the area showing no PL and about 1500–2000 Å for the area showing weak PL.

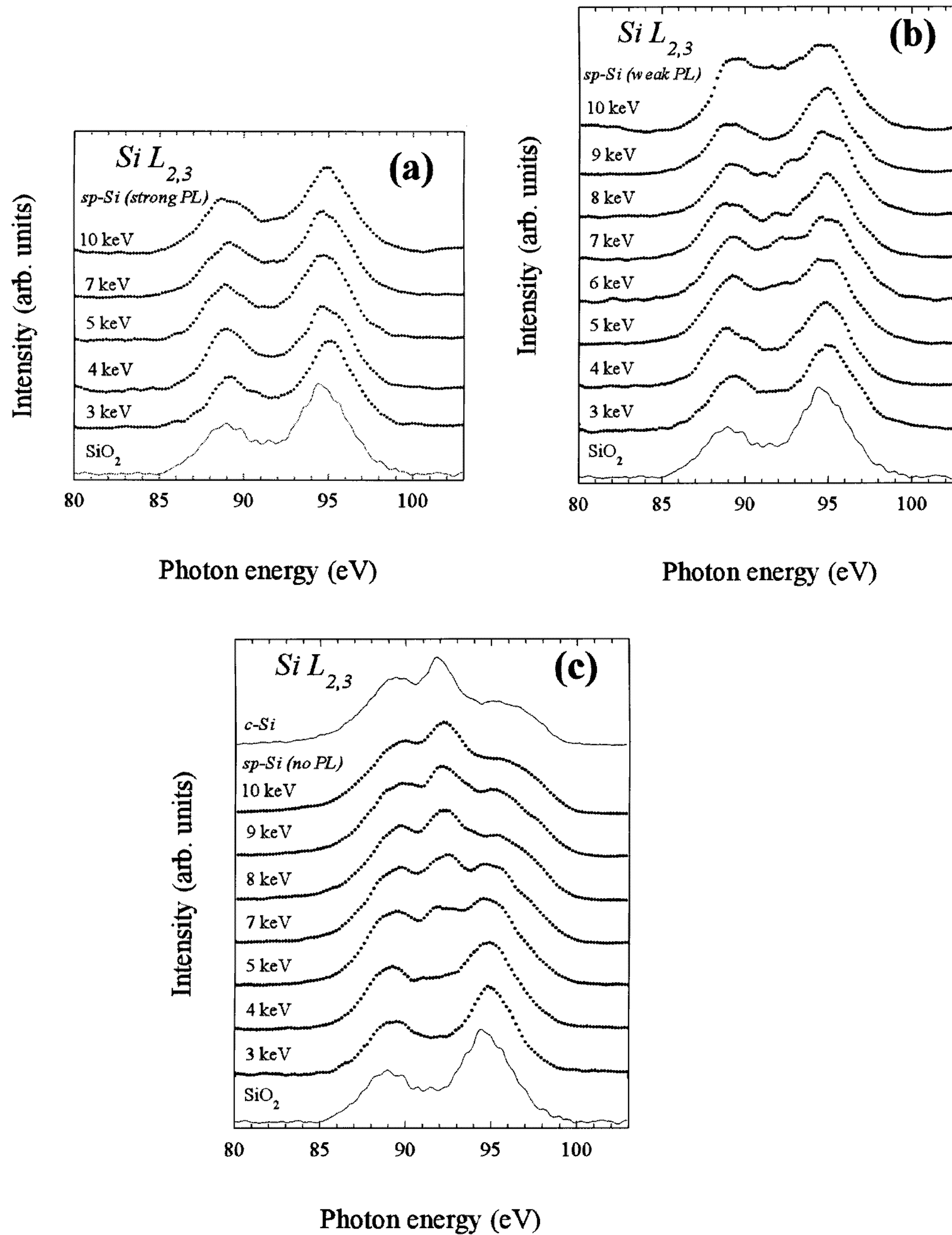

Figure 5. Si $L_{2,3}$ XES of sp-Si for areas with strong PL (a), with weak PL (b), and without PL (c) measured at $E = 3$–10 keV. The Si $L_{2,3}$ spectra of c-Si and SiO_2 are shown for comparison.

Si $L_{2,3}$ spectra for sp-Si processed in *stagnant* and *flowing* air are compared in figure 6. In both cases the spectra show two peaks (A and B). The energy positions of these subbands and the intensity ratio are close to those of SiO_2. This means that Si atoms are oxidized during or after *spark* processing. The spectra do not show any noticeable changes with electron excitation energy from 4 to 10 keV. Consequently, oxidation of sp-Si is not

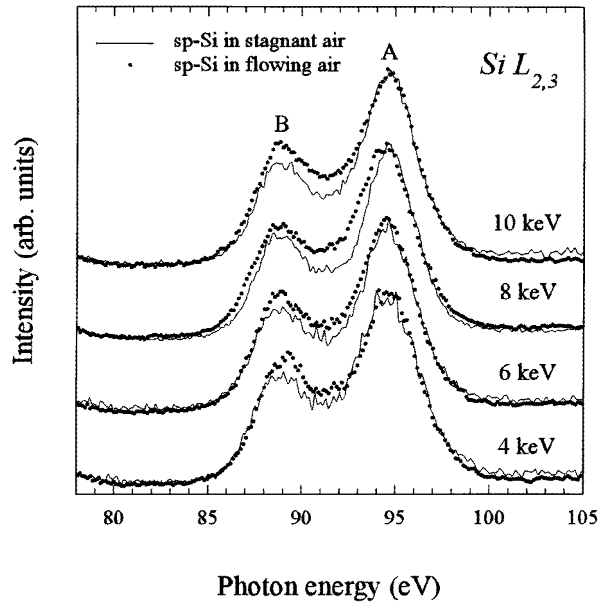

Figure 6. Si $L_{2,3}$ XES of sp-Si prepared in flowing air showing blue PL (points) and in stagnant air, displaying green PL (line). The spectra are measured at 4, 6, 8, and 10 keV.

solely a surface property, but also takes place in the bulk of the sample.

It is interesting to note that the intensity ratio I_A/I_B is less for the specimen prepared in *flowing* air than for that processed in *stagnant* air. According to the measurements of the Si $L_{2,3}$ spectra of SiO_x with x ranging from 0.3 to 2.0 (see reference [24]), the relative intensity of peak B decreases with x. In other words, the oxygen content is less for sp-Si prepared in *flowing* air than for that prepared in *stagnant* air. This is a surprising result as one would assume an opposite proportion, because preparation in flowing air should provide an excess of oxygen. For an explanation we favour the following consideration which is based on the experimental results of Hosono and Matsunami [28] on structural defects in SiO_2 induced by oxygen-ion implantation. They observed an increased generation of a defect type which is characterized by direct Si–Si bondings (oxygen vacancies) concomitant with the implantation of oxygen into SiO_2. During *spark processing* in *flowing* air, silicon oxides are formed first, having a stoichiometry near to SiO_2. During the ongoing spark process, additional oxygen ions are accelerated towards the silicon oxide and may thus generate the above-described oxygen vacancy defects as well as interstitial oxygen.

Interstitial oxygen can be expelled by heat treatments below 500 °C from SiO_2. As the PL of sp-Si is stable for annealing up to 800 °C [32] one can conclude that this type of defect is not correlated with the luminescent centres. During the spark processing itself the localized temperature at the impact spot is assumed to be much higher, thus supporting the assumption of an outdiffusion of interstitial oxygen and an enrichment of Si–Si bond defects. Similar Si backbone structures from Si polymers are known to luminesce in the UV and visible part of the spectrum [33]. These Si-based macromolecules are assumed to have a direct-type band structure with optical transitions allowed between σ and σ^* states of the Si skeleton. The weak thermal stability of Si polymers is mainly caused by the dissociation of Si bonds to OH or organic molecules. However, for sp-Si the Si–Si molecules are more

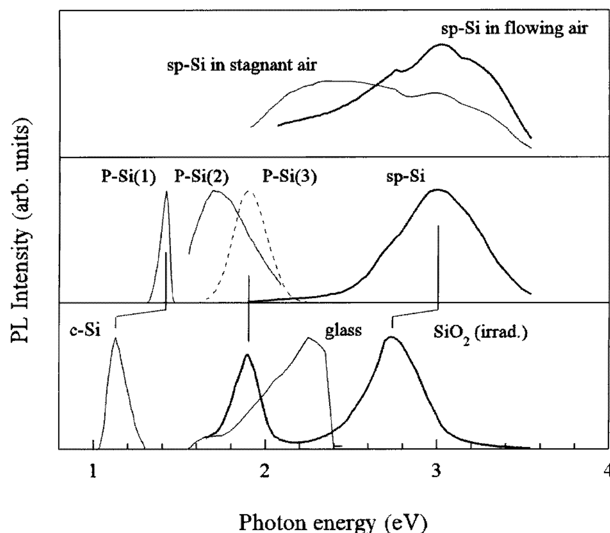

Figure 7. Upper panel: PL spectra for sp-Si prepared in *stagnant* air (thin line: present paper) and in *flowing* air (thick line: present paper); middle panel: PL spectra for P-Si(1), P-Si(2) (solid line [11]), and P-Si(3) (the latter spectrum has been taken from reference [10]); lower panel: PL spectra of c-Si [11], glass [5], and SiO_2 after irradiation [31].

probably bonded to substituents like oxygen or nitrogen, and are thus much more stable against heat treatments.

Photoluminescence spectra of *porous* and *spark-processed* silicon are compared in figure 7. For P-Si(1) a narrow line at energies between 1.30 to 1.46 eV is observed only at temperatures below 40 K. Its intensity is very low. This peak is shifted by about 0.3 eV towards higher energies when compared with the band–band transition of c-Si, and derives probably from a *quantum confinement* effect in nanometre-sized structures of *porous* Si [11]. The Si $L_{2,3}$ spectrum for this specimen (see figure 2) suggests that mostly local Si–Si bonds are present. This finding can be related to the presence of amorphous Si (see figure 3) or, alternatively, to contributions from Si nanocrystallites which are possibly subject to quantum confinement. The latter effect raises the lowest possible electron states in the conduction band and lowers the highest energy levels in the valence band. Such a shift in the valence band edges of *porous* Si of about 0.46 eV has been reported recently using x-ray fluorescence Si $L_{2,3}$ spectra [29]. Unfortunately, reference [29] does not include PL spectra of the samples under investigation.

For P-Si(2), a much wider PL band is observed, extending over the energy range between 1.49 and 2.10 eV [11] (see figure 7). This band resembles the usually observed red–yellow PL. The exact peak position within this energy range depends on the preparation conditions [2]. In figure 7 two red PL bands of porous silicon are presented. The data for sample P-Si(2) were taken from reference [11] and those for P-Si(3) from reference [10]. It is evident (see figure 7) that the PL bands for P-Si(2) and P-Si(3) are similar to the red PL band of SiO_2 with defects induced by irradiation [30, 31] (see the PL bands of SiO_2 (irrad.) in the lower panel of figure 7). This suggests that chemical bonds are mostly local Si–O bonds, which is in good agreement with the observation of the local Si–O bonds from Si $L_{2,3}$ XES. Thus, we can conclude that these red–yellow PL bands of porous silicon are more appropriately described by a defect picture in contrast to the *quantum confinement* model.

For sp-Si, intense PL bands are observed in the green as well as the UV/blue region of the spectrum [8–10]. They do not coincide with defect-related PL bands of SiO_2 which was subjected to radiation. The dominant contribution for the present XES spectra stems from Si–O bonds. It is necessary to point out that Si nanocrystallites, which were observed in sp-Si [9–10], cannot be detected by XES.

4. Summary

We have found by using x-ray emission spectroscopy that the local structure of *porous* silicon prepared from p^+ Si is inhomogeneous and consists of a mixture of c-Si, a-Si, and $SiO_{0.30}$. Silicon prepared by the anodizing of n^- Si and exposed to air over a two-year period is oxidized to a much higher extent. The degree of oxidation is close to that of SiO_2. Both the local structure and the oxidation effects were found to be independent of the depth down to 10 000 Å.

Specimens which show a visible luminescence in the red and green–blue spectral regions are generally characterized by a high content of Si–O bonds. On the other hand, *porous* Si with PL peaking in the infra-red region between 1.30 to 1.46 eV the Si $L_{2,3}$ x-ray emission spectra are very similar to those of c-Si.

It is found that the Si $L_{2,3}$ x-ray emission spectra of *spark-processed* silicon depend on the position on the treated area. For areas having strong PL, a strong oxidation on the surface (SiO_2) was observed. The thickness of the oxidized layer was estimated to be not less than 10 000 Å. For areas having weak or no PL, the amount of oxygen on the surface as well as the depth of oxidation continuously decrease. A higher degree of oxidation is observed for Si spark processed in stagnant air when compared to that prepared in flowing air. This finding is probably related to the generation of Si–Si bond defect states by oxygen implantation.

Acknowledgments

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