

## Surface photovoltage spectroscopy of porous silicon

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Results of surface photovoltage spectroscopy on free-standing porous silicon films fabricated from boron-doped Si wafers of various resistivities are presented. We find that all the films have bandtails, which are about 0.3 eV wide, and their optical band gap is about 2 eV. The majority carriers in the strongly luminescent and poorly photoconducting films are holes, while in the weakly luminescent but photoconducting films they are electrons. This difference between the films appears to be due to different oxygen coverage of the silicon nanocrystallites. We conclude that the origin of the strong red-light luminescence is in the electron optical transitions from the conduction bandtail to the valence bandtail. [S0163-1829(97)50604-7]

Despite extensive efforts,<sup>1</sup> the nature of the visible photoluminescence (PL) from porous silicon (PSi), whether due to the geometrical and quantum confinement in the Si crystallites, to surface states, or to various silicon compounds, is still intensely debated.<sup>1,2</sup> While there is strong evidence that the PL originates from the crystallites,<sup>3</sup> the difference of about 0.3 eV between the optical absorption band gap  $E_g$  and the red PL,<sup>4-6</sup> as well as the effect of “chemical” treatments on the PL,<sup>7,8</sup> indicate that it is not the conceptually simple radiative band-to-band process. In fact, optical absorption measurements do not yield a clear answer concerning the nature of the band gap,<sup>6,9</sup> and the type of the majority carriers in luminescent PSi has not been identified. This is manifested by the fact that while very many works suggest the presence of bandtails<sup>6,10,11</sup> there is very little direct evidence<sup>12</sup> for their existence, and there were only very few attempts<sup>6,9,11</sup> to determine their widths. In particular, as far as we know, no attempt was made to distinguish experimentally between the valence bandtail and the conduction bandtail. It is also customary to call the PSi,  $p$ -type or  $n$ -type according to the type of wafer of which it was formed rather than to carry out a direct test of the type of the PSi layer. Again, very few attempts<sup>13,14</sup> have been reported for such a test and in those cases no correlation was made to the efficient photoluminescence.

Following these considerations we have carried out a comprehensive study of surface photovoltage spectroscopy<sup>15-17</sup> (SPS) of PSi films that were prepared on  $p$ -type crystalline Si ( $c$ -Si) wafers. We note that this method is particularly suitable for resolving the above-mentioned issues (see below), while, as far as we know, there has been only one previous application<sup>18</sup> of the SPS technique to PSi. However, in that case the PSi layer was not removed from the  $c$ -Si substrate, and thus, because of the contributions of the substrate and the substrate-PSi interface barrier<sup>19</sup> the results were not suitable for the above suggested analysis (see below). Indeed, no analysis and no interpretation have accom-

panied that study. For further characterization of the PSi layers used in the present study, we have measured the photoluminescence,<sup>20</sup> the dark and photoconductivity,<sup>21</sup> and the Raman spectra<sup>22</sup> of the present PSi layers, using these techniques in the modes that we have described previously.

In the SPS method<sup>15</sup> one measures the change, induced by illumination, in the contact potential between a metal plate (the Kelvin probe) and the semiconductor surface. This change  $U$ , which is the surface photovoltage, is monitored as a function of the light photon energy  $h\nu$ . The corresponding subband-gap absorption, which results in electron transitions to and from localized states, causes a change in the electrical charge in such states. Charge neutrality is maintained by a change in the space charge, i.e., by the band bending. In an  $n$ -type material, under the usual electron depletion conditions near the surface, photoelectron excitation from a localized state to the conduction band causes band “flattening” yielding a negative  $U$ . Hence, in an  $n$ -type material,  $U$  decreases when  $h\nu$  equals the energy separation between the conduction-band edge and a localized level. Since the electron concentration at the valence-band edge is very high, once  $h\nu$  is larger than the band gap,  $U$  saturates.<sup>16</sup> Similarly, for a  $p$ -type material under hole depletion, electron transition from the valence band to an electron empty state yields a “flattening” of the bands and thus a positive  $U$ . In particular, the sharpness of the  $U$  variation with increasing  $h\nu$ , as  $h\nu$  approaches the band-gap energy  $E_g$ , reflects the sharpness of the valence-band edge in an  $n$ -type material and the sharpness of the conduction-band edge in a  $p$ -type material.<sup>17</sup> Hence, the SPS provides among other data both the width of the bandtails and the type of semiconductor. The SPS measurements, the results of which will be given below, were carried out as described previously.<sup>17</sup> In particular, we should point out that this measurement was carried out at room temperature and in air ambient.

The samples for our study were fabricated from boron-doped Si (100) wafers that were anodized, as previously

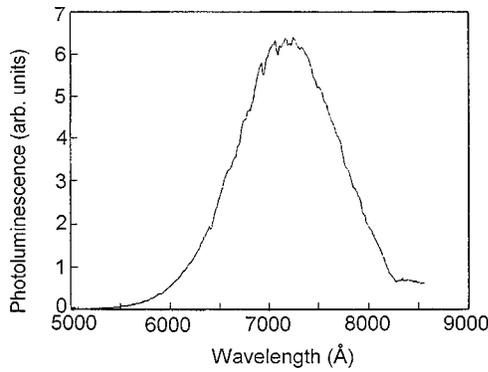


FIG. 1. The PL spectrum of a sample of set A.

described,<sup>20</sup> by a (25% HF)/(75% water) solution with an anodizing current density of 143 mA/cm<sup>2</sup>. Samples of set A were anodically etched (for 10 min) high-resistivity (7–20 Ω cm) crystalline silicon (*c*-Si) wafer; samples of set B were anodically etched (for 12 min) from a low-resistivity (0.01–0.02 Ω cm) wafer, and samples of set C were anodically etched (for 10 min) at a current of 107 mA/cm<sup>2</sup> from another high-resistivity (7–17 Ω cm) wafer. Following the anodic etching, the samples were rinsed with distilled water and allowed to dry. In order to eliminate the contribution of the *c*-Si substrate to the measured surface photovoltage and the conductivity, “free-standing” films were required (see below). While drying, samples of set A flaked off spontaneously to yield such films. As samples B and C did not flake off, they were reetched for 5 min at 143 mA/cm<sup>2</sup> and then rinsed. Following the second etching, parts of the PSi layer flaked off. The free-standing flakes were as large as 1 cm<sup>2</sup>. Their thicknesses were all measured to be 5 μm. Our corresponding Raman spectra<sup>22</sup> were all typical of samples<sup>23</sup> of 3–4 nm nanocrystals.

The efficient ( $\eta \sim 1\%$ ) PL spectrum of a typical flake of set A is shown in Fig. 1. In agreement with our recent<sup>20</sup> and many other studies,<sup>1–9</sup> the strong featureless red emission peaks were observed at a wavelength  $\lambda$  of 720 nm (photon energy  $h\nu \approx 1.7$  eV). The peak of the emission of set C samples was at similar  $\lambda$ , but  $\eta$  was ten times smaller. The emission from set B samples was hardly detectable, but also peaked at a similar  $\lambda$ .

Figure 2(a) presents the typical  $h\nu$  dependence of the surface photovoltage  $U$  of the “parent” Si substrates of all wafers. Features beyond  $h\nu = 2.7$  eV are of little relevance to the present discussion. The observed  $U(h\nu)$  dependence is typical<sup>16</sup> of *p*-type *c*-Si. The sharp rise followed by the saturation of  $U(h\nu)$  corresponds to the onset of the band-to-band transitions (generation of electron-hole pairs) at the 1.1-eV indirect gap of *c*-Si (which is indicated by  $E_g$  in this figure). This behavior results from the photoinduced reduction in band bending of the initially hole-depleted surface region of the *p*-type material.<sup>15,16</sup>

The SPS of a PSi film of set B, which was retained on top of its “parent” wafer, is shown in Fig. 2(b). While the  $U(h\nu)$  dependence is the same as that of the substrate wafer, the magnitude of  $U$  is different [Fig. 2(a)]. This implies that the photon absorption and carrier excitation occur mainly in the *c*-Si substrate, but that the change in the magnitude of  $U$  is induced by the photocarriers that reduce the band bending at

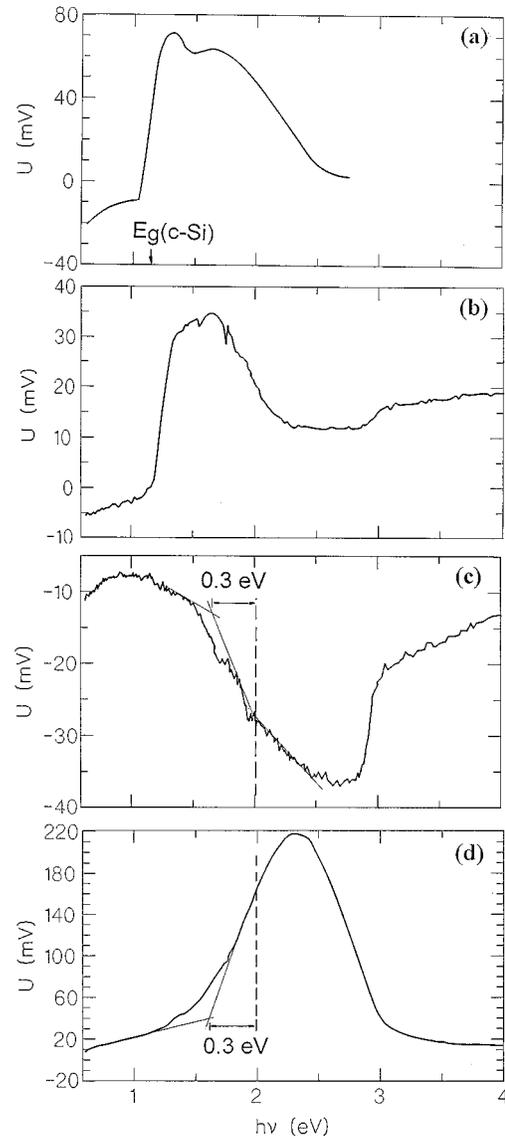


FIG. 2. Typical dependence of the photovoltage on the excitation-photon energy for the *p*-type *c*-Si substrate of set B (a), a PSi layer on a *p*-type *c*-Si substrate of set B (b), a free-standing film derived from a sample of set B (c), and on a free-standing film derived from a sample of set A (d).

the PSi surface. Therefore, the similar  $U(h\nu)$  dependence masks the optical absorption contribution of the PSi layer to the observed  $U(h\nu)$ . It is thus apparent that in order to obtain a reliable spectrum of the PSi-only material, free-standing films of PSi must be employed.

Figure 2(c) displays the spectrum of the free-standing flakes of set B. Indeed, this spectrum is very different than the one shown in Figs. 2(a) and 2(b). The spectrum exhibits an *n*-type rather than a *p*-type behavior and shows that the “normal” *c*-Si ( $E_g = 1.1$  eV) absorption is totally absent. These differences demonstrate the erroneous conclusions that may be drawn from measurements that are carried out on PSi layers when these are attached to the substrate. The fact that the free-standing flakes behave as expected for an *n*-type semiconductor<sup>15–17</sup> (see above) shows that an *n*-type PSi can result from a *p*-type wafer. The fact that we and other authors<sup>13,14</sup> (using other techniques) find such a phenomenon

indicates that one *cannot* assume *a priori* that the type of the PSi layer is the same as that of the substrate. In addition to the apparent band gap of about 2 eV (see below), we see that here, for the free-standing (flake only) layer, there is a drop of  $U(h\nu)$  towards the latter energy. The observed drop is seen to be quite gradual when compared to the rise around  $E_g$  for *c*-Si [Figs. 2(a) and 2(b)]. This clearly indicates the presence of a valence bandtail, as we have already discussed for hydrogenated amorphous silicon,<sup>17</sup> *a*-Si:H.

For the derivation of a more quantitative spectroscopic information let us recall that in *c*-Si, when its surface is relatively “pure” the  $h\nu$  value at which  $U(h\nu)$  rises sharply yields the value of  $E_g$ . When there are gap states that lie close to the band edges there is a more moderate rise of  $U(h\nu)$ , with the corresponding threshold shifting to lower  $h\nu$  values. In this case the value of  $E_g$  is better approximated by the intersection point of the tangents to the rise and saturation sections of the  $U(h\nu)$  curve.<sup>16</sup> Turning to disordered semiconductors the existence of bandtail states enables only the latter procedure for the determination of  $E_g$  from SPS data. Hence, we applied this procedure to *a*-Si:H samples and found,<sup>17</sup> by comparison with our optical data (using the Tauc plot), that this procedure yields the correct optical gap in that material. The results in Fig. 2(c) are not as clear as those of *a*-Si:H but are still applicable to the above procedure. Using this procedure and considering the fact that the selection of the tangents is somewhat arbitrary we can derive only a rough estimate for the value of the optical gap. This value appears to be of the order of 2 eV. Since the contribution of the bandtail states is manifested by the  $U(h\nu)$  drop that precedes 2 eV, the bandtail width can be determined by a similar procedure to the one described above, i.e., by finding the intersection of the corresponding tangents. Again, this procedure yielded<sup>17</sup> very reasonable values for *a*-Si:H. Using this procedure in Fig. 2(c) we get then an estimated value of 0.3 eV, for the valence bandtail width.

A typical surface photovoltage spectrum of a flake of a sample from set A is shown in Fig. 2(d). The behavior of  $U(h\nu)$  clearly indicates (see above) that the flakes of set A are *p*-type semiconductors. Again, no evidence for light absorption from bulklike *c*-Si is seen. Here, the determination of  $E_g$  is even more difficult than in Fig. 2(c) but using the same procedure we can get, again, an estimate for the value of  $E_g$  that is also of the order of 2 eV. On the other hand, the derivation of the conduction bandtail width is clear as in Fig. 2(c), and using the same procedure we again get a value of about 0.3 eV.

In the PSi flakes of set C, the spectrum of which is not shown,  $U$  had much smaller values than those of sets A and B. However, a similar but very small rise in  $U$  around  $h\nu=2$  eV was observed. This behavior can be consequently described as that of a “slightly” *p*-type semiconductor.

The foregoing results demonstrate that the strong luminescence occurs in a *p*-type material that has a conduction bandtail width of  $\sim 0.3$  eV. It also suggests that the transition from the strongly luminescent films of set A, through those of set C, to the weakly luminescent films of set B is accompanied by a transition from *p*- to *n*-type behavior. Such a behavior is most likely due to the increase in the nonradiative recombination paths<sup>24,25</sup> as the film becomes an *n*-type material. In order to check this point we carried out pho-

totransport measurements<sup>21</sup> under a He-Ne laser photon flux of  $10^{17}$  photons/cm<sup>2</sup> s. We found that in the temperature range from 300 to 400 K the values of the dark conductivity  $\sigma_d$  and the photoconductivity  $\sigma_{ph}$  of the flakes from set B ranged from  $10^{-6}$  to  $10^{-5}$  ( $\Omega$  cm)<sup>-1</sup> when exposed to air. The values of  $\sigma_d$  and  $\sigma_{ph}$  of the flakes of set A were below our detection limit, while the values of set C were ten times smaller than those of set B. Hence, the samples of set C were intermediate between those of sets A and B, in both their SPS and transport properties. This anticorrelation between the PL intensity and  $\sigma_{ph}$  is expected and similar to the one found in *a*-Si:H.<sup>26</sup>

To evaluate the reason for the different conductivities of the various samples we have turned to a “low-temperature” chemical treatment of the samples, which may affect gas adsorption but is not expected to affect the crystallite sizes in the PSi. This “treatment” consisted of decreasing the sample ambient pressure down to  $10^{-5}$  Torr at room temperature. For the conducting samples of set B, both  $\sigma_d$  and  $\sigma_{ph}$  were completely suppressed, and (similar to the effect of methanol<sup>25</sup>) the reexposure to air restored these conductivities almost completely. This behavior is clearly due to the variation in the oxygen and/or water surface coverage of the PSi structure and is not due to any variation in the PSi particle size. It therefore appears that, in agreement with previous suggestions for PSi, and as found<sup>27</sup> in *a*-Si:H, the adsorbed oxygen and/or water plays the role of a donor<sup>24</sup> as well as a weak-bond breaker.<sup>20</sup>

The above-described transition from a nonconducting luminescent material to a conducting nonluminescent material of the same band gap suggests that the three sets of samples are not radically different semiconductors (e.g., that one is composed of quantum-confined nanoparticles and the other of siloxenelike compounds). Rather, the basic electronic structures of all our PSi samples appear to be the same. The difference must therefore lie in their defect structure that determines the radiative vs nonradiative recombination paths, as well as the type of majority carriers. The origin of these defects is in oxygen or water molecules that yield donor states and nonradiative recombination centers.

Let us now discuss the strong red emission around 1.7 eV and our results in view of two major reported findings. (i) Resonant PL measurements show that the radiative transitions occur in the crystallites.<sup>2,3</sup> (ii) The featureless red emission band of PSi is very similar<sup>2</sup> to that of *a*-Si:H, for which it has been established<sup>28</sup> that radiative bandtail-to-bandtail transitions are responsible for the 1.4-eV PL, while  $E_g=1.7-1.8$  eV. These findings suggest that the strong red luminescence of PSi is due to radiative transitions between the conduction bandtail and the valence bandtail states of the crystallites for which the usual crystal-momentum selection rules are relaxed, due to the small size of the crystallites.<sup>29</sup> Such a relaxation was already suggested years ago for the phonon-excitation spectra in nanocrystallites.<sup>30</sup> While the bandtail states in *a*-Si:H are strictly due to disorder, in PSi there may be a combined effect of size (e.g., due to crystallite size variation<sup>2,3,6,29,31</sup>) and disorder. In any case, the outcome appears to be essentially the same, i.e., a much more efficient luminescence than for the indirect gap of *c*-Si. The suggestion that the luminescence takes place within the crystallites accounts well for the much higher efficiency of the

PL in PSi in comparison with that of  $a$ -Si:H,<sup>27</sup> in spite of the similar origin of the radiative transitions. This is because the crystallites provide the geometrical (i.e., the potential barrier<sup>31</sup>) confinement of the excited electron-hole pairs. Support for this suggestion is given by the fact that in systems of isolated nanocrystals<sup>32</sup> the PL efficiency is higher than in PSi. Thus, we may conclude that “physically,” PSi is “intermediate” between a nanocrystalline system and an  $a$ -Si:H-like system. This also explains the sensitivity of the PL to the details of the PSi structure that can make the material more nanocrystallinelike or more  $a$ -Si:H-like. In particular, the much debated effect of oxygen,<sup>1-3</sup> for which we gave an example in this paper can drive the systems in either direction. The exposure to oxygen may yield an oxide shell that increases the isolation of the crystallites by providing a wider potential barrier. At the same time it can also provide nonradiative recombination paths by creating new/more sur-

face states, such as by breaking weak Si-Si bonds.<sup>20</sup>

In conclusion, it is suggested that bandtail-to-bandtail transitions (in which the momentum selection rules are relaxed) and the geometrical-potential confinement of the excited electron-hole pairs are responsible for the strong red PL in PSi. Further studies aimed at determining the various sources of the bandtail states and the carrier relaxation mechanisms within them, should shed light on the detailed nature of the PL in PSi.

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