Local environment of Boron impurities in porous silicon and their interaction with NO$_2$ molecules

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The aim of this paper is to gain insight into the observed recovery of electrical activity of B impurities occurring in Porous Silicon (PS) layers exposed to NO$_2$ molecules, while addressing the problem of the origin of B passivation in PS. Two possible mechanisms are considered, i.e., that the extra electron needed for the fourfold coordination of B atoms be provided either by H atoms (through the formation of Si-H-B complexes) or Si dangling bonds at the surface. Experimental evidence shows unambiguously that a negligible amount of B atoms binds with H, even in posthydrogenated PS, the main passivation source being the Si surface dangling bonds. This explains both the mechanism of formation of PS under electrochemical etching and the efficiency of the NO$_2$ molecules in restoring conduction.

I. INTRODUCTION

The recent observation of efficient free-carriers generation in p^+ porous silicon (PS) when exposed to NO$_2$ molecules[1–3] suggests that this material in particular conditions can behave as a real semiconductor, such as the starting c-Si substrate. This effect has been observed only in PS layers with high amount of B impurities.[1,2] In spite of this, the PS layers behave as insulators. This suggests that B atoms passivation is the key mechanism for the lowering of PS conductivity, but also that such passivation is reversible. In fact B acceptors can be "switched on or off" by simple exposure or removal of the sample to NO$_2$. The aim of this work is to understand the environment of B impurities in PS in order to explain the high resistivity of p^+ mesoporous silicon and the impressive repopulation of the material in presence of NO$_2$ molecules. FTIR (Fourier transform infrared) and Raman spectroscopies together with TPD (thermal-programmed desorption) measurements have been performed for the purpose.

High values of resistivity and carriers freeze-out in p^+ mesoporous silicon has been reported in the past[4,5] and explained in terms of surface effects. Quantum-confinement effects, even if cannot be totally excluded, are not presumably the main contribution to carrier depletion, since the typical skeleton-size distribution of this material ranges between 4 and 12 nm.[6] As far as the crystalline counterpart of p^+ PS is concerned, B passivation has been observed in the past to occur through the formation of Si-H-B complexes (see Ref. 7 for a review). Spreading resistance,[8] FTIR (Ref. 9) and *ab initio* calculations[10] demonstrated that this compound can effectively reduce the doping efficiency of B up to 99%. It seemed to us, thus, straightforward to consider Si-H-B complexes as possible candidates for B passivation in PS, taking into account that, in principle, it is possible to have a substantial amount of H in PS, as a consequence of the anodization process.

Grosman and Ortega[11] did not report the presence of the IR mode of the Si-H-B compound at 1875 cm^{-1} on free-standing PS layers. In contrast, they observed this band on samples still lying on the original substrate: this led them to conclude that Si-H-B compounds are present only in the bulk Si region close to the PS interface. When the etching front proceeds, these complexes disappear and some other kind of B passivation takes place. Other authors[12] reported an increase of conductivity of p^+ PS after annealing at 150 °C–200 °C, the typical temperatures at which the Si-H-B compound dissociates.[9] This indirect observation led them to conclude that such complex plays an effective role in passivating B atoms in PS.

II. EXPERIMENT

In order to ascertain which of the above hypotheses is correct (either surface effect or Si-H-B formation), we carried out a detailed IR spectroscopic study on both as-prepared and hydrogenated PS membranes from p^+ substrates (5 mΩ cm resistivity). The membranes, 300 μm thick and showing a porosity around 60%, have been obtained by introducing etch stops in order to replenish the solution inside the pores so avoiding the vertical porosity gradient,[13] and detached by means of a high-current pulse at the end of anodization. Some of the samples have been subjected to posthydrogenation, obtained by exposing the membranes to a H$_2$ plasma for 90 min at a pressure of 2.4 mbar. By means of this method we were able to passivate the B atoms for a depth of ≈ 2 μm from the surface in p^+ c-Si samples, with an increase of the sheet resistivity of two orders of magnitude and the reduction of Fano resonances in first order Raman spectra.[9]

As previously mentioned, the Si-H-B complex is known to dissociate at temperatures around 150−200 °C.[9,12] The release of gases from the as-prepared sample because of programmed heating in inert flow is reported in Fig. 1, both as desorption of H$_2$ (mass-spectrum data) and total effusion (gas conductivity measurements). The major part of effused
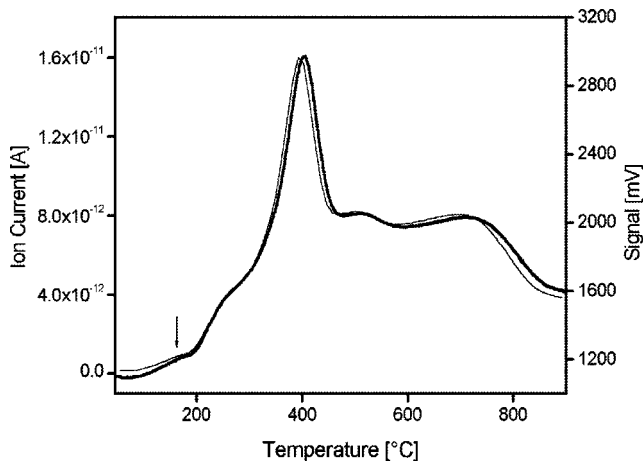
FIG. 1. TPD (Effusion) curves from a porous silicon membrane. Thin curve is the signal from a quadrupole mass analyzer centered onto the H_2 mass (left scale). Thick curve shows the thermal conductivity signal, i.e., the total amount of desorbed gases (right scale). The two curves have been superimposed, to show how the major contribution to effusion comes from H_2 molecules.

molecules are H_2 even if a small contribution from silanes has been observed. Basically this process takes place at temperatures above 350 °C, and only a negligible amount of H_2 is desorbed at 150–160 °C. This strongly suggests that the concentration of Si-H-B centres is low.

Figure 2 compares the IR spectra concerning a 120-μm-thick membrane, as-prepared (curve 1) and after TPD treatment up to 180 °C, temperature at which the Si-H-B species present have been depleted (see the arrow in Fig. 1). An absorption increase, due to free-carriers population is observed.[14] By fitting the absorption baseline by means of the Drude model[15] the following free-carrier concentrations are found: 2×10^{17} cm^{-3} and 3×10^{17} cm^{-3} for the as-prepared and the thermally treated samples, respectively. Assuming, for semplicity that the original B concen-

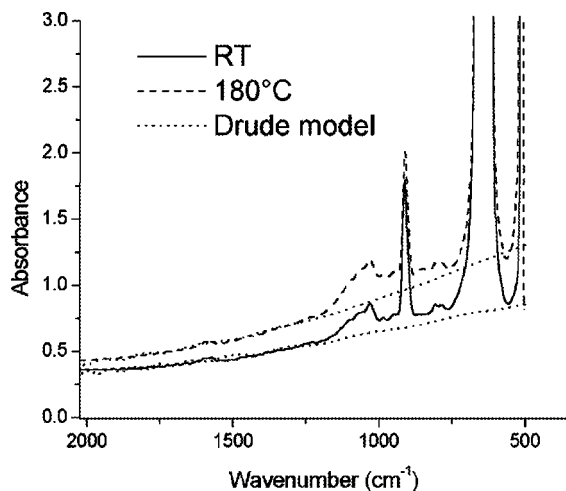FIG. 2. FTIR spectra from a 120-μm-thick PS membrane before (lower curve) and after (upper curve) H_2 outgassing in vacuum at 180 °C. The Drude fits of the spectra baselines are also displayed.
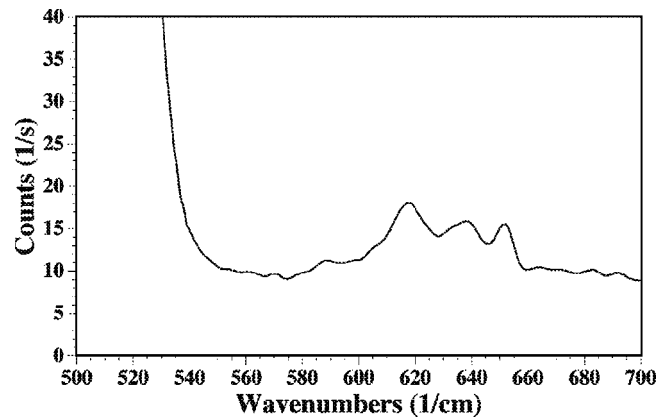

FIG. 3. Raman spectrum from a PS membrane. See text for details.

tration (3×10^{19} atoms cm^{-3}) is conserved after anodization, the value 2×10^{17} cm^{-3} suggests that 99% of B atoms are passivated in p^+ mesoporous Si. Among them, less than 1% is passivated through the formation of Si-H-B, as the increase in free-carriers concentration caused by thermal treatment is only 1×10^{17} cm^{-3}. The formation of such complex is then much less probable than the formation of other hydrogenated structures. Moreover, attempts to detect the corresponding vibrational peak at 1875 cm^{-1}, assigned to the Si-H stretching mode in the Si-H-B complex, even in relatively thick (300 μm) both as-prepared and plasma-hydrogenated membranes did not provide any clear signature for such vibrational mode, indicating that its intensity is below the sensitivity of the technique. Thus, it can be concluded that added H does not form preferentially the Si-H-B complexes. This further confirms that B atoms in PS are already passivated in some other way. Support to this conclusion also comes from Raman spectra of as-prepared membranes, under 488 nm illumination. No signature of Si-H-B compounds is observed. Instead, as Fig. 3 shows, B modes are clearly visible at 620 cm^{-1} and 640 cm^{-1}, together with a peak at 652 cm^{-1} that has been interpreted in the past as related to the loss of symmetry of the B center because of the presence of a neighboring H atom.[9] An alternative assignment, together with other features will be the subject of a forthcoming paper.

III. DISCUSSION

Some other mechanism has to be found to explain the 99% efficiency of passivation of B atoms in p^+ PS. To passivate substitutional B in Si, an extra electron is needed, in order to complete its fourfold coordination. Our results indicate that such an electron is not provided in PS by H. On the other hand, Si dangling bonds can provide the extra electron needed to passivate B atoms, through the relation[16]

$$B_3^0 + D^0 \rightleftharpoons B_4^- + D^+. \tag{1}$$

Since in PS dangling bonds are expected to be at the surface, B impurities are thought to be located underneath. In

fact, surface B atoms are likely to have a stable trigonal coordination, and, therefore, to be totally electrically inactive, so that it would be possible to explain neither passivation of B impurities nor the above-mentioned "on-off" effect with NO$_2$. The model advanced here agrees well with the mechanism proposed by Polissky and coworkers,[17] who explained the observed percent increase of B atoms consequent to anodization by proposing a selective etching mechanism. When the etching front approaches the boron impurity located immediately underneath the surface, this looses its acceptor character and cannot provide the hole necessary to further sustain the etching. The Si atoms removal is then stopped and etching proceeds elsewhere.

Intimate pairs between a doping impurity and a Si dangling bond have been observed in a-Si:H (Ref. 18) and the energy location in the a-Si:H band diagram of the reaction products in Eq. (1) has been calculated.[16] The formation of such complex is one of the different mechanisms able to neutralize dopant impurities in a-Si:H. Another mechanism is the above-mentioned Si-H-B complex, which has been found not to be operative in PS. Finally, substitutional dopant impurities have a strong tendency to enter the Si random network in the form of threefold-coordinated, electrically inactive, alloying sites.[19] PS from p^+ substrates is found to be mainly crystalline[20] and the last mechanism has to be ruled out.

Impurity passivation in p^+ PS occurs through the transfer of an electron from a dangling bond to an acceptor. This mechanism is always thermodynamically favourable,[21] i.e., in equilibrium conditions. Even if there is no experimental proof for intimate pair formation in PS, equation (1) holds also for larger distances between the dangling bond and the impurity. Work is in progress to ascertain the presence of intimate pairs in p^+ PS. Moreover, according to the formation model proposed in Ref. 17, there is a high probability for a B atom to interact with a dangling bond in PS: this could be the reason why this mechanism is preferential in PS.

Using first-principles self-consistent pseudopotential calculations in conjunction with a supercell model for the amorphous network, authors of Ref. 16 showed that the interaction between the neutral dangling bond, originally located at midgap, and the B impurity gives rise to a charged dangling bond (D^+) whose energetic location is close to midgap, and B_4^- that merges into the valence band. According to Eq. (1), the Fermi level in the $B_3^0 + D^0$ configuration is pinned at midgap by the D^0 states. It shifts downwards upon conversion to the $B_4^- + D^+$ configuration, but, because of the creation of a defect coincident with the creation of a doping state, it cannot shift below the band of acceptor states and the material behaves like an intrinsic one. When NO$_2$ interacts with the surface of PS, acceptorlike states are formed. The Si-NO$_2$ complexes can be considered either as acceptor states *per se* or as surface states giving rise to upward band bending.[15] The absence of carrier repopulation in lightly doped PS suggests us to neglect the first hypothesis. When the energy bands are shifted upwards on the surface, locally
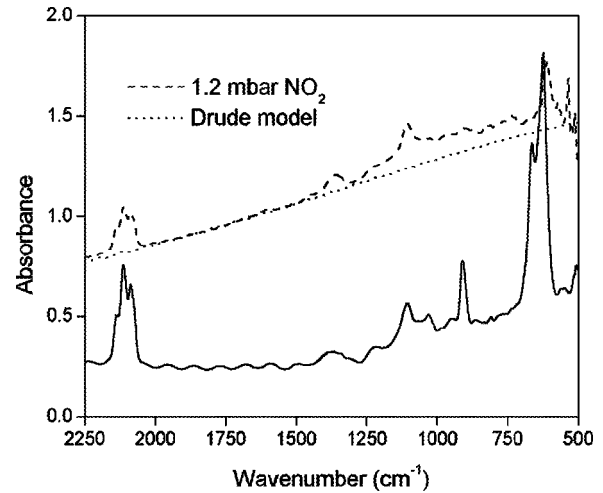

FIG. 4. FTIR spectra from a 40-μm-thick PS membrane in vacuum (lower curve) and under NO$_2$ exposure ($\approx$1.2 mbars, equilibrium pressure). Note that in spite of the much lower membrane thickness (40 μm instead of 120 μm), absorbance values comparable to those of Fig. 2 are obtained thanks to NO$_2$ exposure.

the Fermi level can shift below the B_4^- band and the original acceptor character of B is restored.

A charge-transfer mechanism implies a 1:1 correspondence between the number of adsorbed NO$_2$ molecules and free holes inside the material. This kind of check is not trivial, because the number of adsorbed molecules is, at the moment, unknown. Attempts to measure it volumetrically showed that it is small, at the most of the order of the B atoms. In contrast, it is straightforward to estimate the number of free carriers from the IR spectra, through the Drude approach used above, under NO$_2$ exposure. Curve reported in Fig. 4 comes from a 40-μm PS membrane under $\approx$1.2 mbars of NO$_2$ equilibrium pressure: from the change in the background it is possible to estimate a density of carriers around 2×10^{18} cm^{-3}. If the upper limit for carrier generation under NO$_2$ is assumed for sake of simplicity, to be 10^{19} cm^{-3}, i.e., as many as the B impurities, adsorption of NO$_2$ activates only a fraction of them. This seems to favor the hypothesis of the 1:1 localization of charge, say 1 NO$_2$ molecule is probably able to activate just 1 B atom, in agreement with the results of studies of the interaction of NO$_2$ with PS by means of other techniques to be presented in forthcoming papers.

IV. CONCLUSION

In conclusion, we have provided several experimental proofs for the negligible role played by H in passivating impurities in PS, suggesting a direct interaction between acceptors and surface dangling bonds. The electronic state of tetracoordinated B is assumed (as in the case of a-Si:H) to merge into the valence band, becoming electrically inactive. This not only explains some features related to the PS formation, but it also explains the spectacular carrier repopulation during NO$_2$ exposure.

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