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Defects in porous p-type Si: An electron-paramagnetic-resonance study

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The defects in p^+ porous silicon of low and high porosity have been studied by using electron-paramagnetic-resonance (EPR) spectroscopy and compared with an impurity analysis obtained from nuclear reaction analysis (NRA). The EPR measurements show, in both high- and low-porosity samples, the same dominant paramagnetic defect which we have identified from its g tensor and hyperfine tensor as the trigonal (111) P_b center; the neutral dangling bond at the Si/SiO$_2$ interface. The symmetry of the central Si hyperfine-interaction tensor has been determined. From the defect concentration it is estimated that about 50% of the surface of p-type porous Si exposed to air is oxidized. The symmetry of the EPR spectrum of the P_b center relative to the substrate proves the monocrystalline character of the oxidized surface with a preferential (111) orientation. In as-grown and aged samples a high fraction (>0.95) of the P_b centers are passivated by H. They are depassivated by a thermal anneal at 400 °C under ultrahigh vacuum, revealing total P_b-center concentrations of some 10^{11} cm^{-2}. Independent of porosity both types of sample were found, by using NRA, to be heavily contaminated by H, C, and O with impurity-atom to Si-surface-atom ratios of 0.3 to 0.6, 0.1, and 0.01, respectively. The 80%-porosity samples, the only ones showing room-temperature visible photoluminescence, contain, in addition, amorphous Si inclusions; their presence is deduced from the observation of the $g=2.0055$ dangling-bond centers in thermally annealed samples. As P_b centers are recombination centers, efficient photoluminescence in 80%-porosity samples, in which surface properties are predominant, requires a minimization and stabilization of these defects.

INTRODUCTION

The recent discovery[1,2] of efficient visible photoluminescence at room temperature in porous silicon has given rise to numerous studies concerning the origin of this light emission and its relation to structural properties of the material.[3] The porosity of the material is one important parameter as it has been shown that the quantum confinement in small Si crystallites[1,2,4] will lead to a shift of the emission into the visible region but alternative models implying the contamination by siloxene[5] and polysilane chains have been proposed equally.[6] Up to now much of the basic information on the structural properties of porous silicon is lacking, such as whether the porous silicon is fully monocrystalline, which are the crystallographic orientations of the internal surfaces, are they covered by hydrogen or by an oxide layer such as SiO$_2$, what is the nature and concentration of interface states, and which is their influence on the photoluminescence properties? Previous ion beam analysis[7] had shown that porous silicon exposed to air is heavily contaminated not only with H but also with O and C in the 10^{15} cm^2 concentration range, but the nature of their incorporation and their relation with the extrinsic photoluminescence models was not determined.

The electron-paramagnetic-resonance technique (EPR) is particularly suited for the studies of bulk, surface, and interface defects in Si and some first results have been published recently.[8-10] However, none of the observed defects has been positively identified. We present in this paper the results of a detailed EPR study on p^+-type porous silicon, which identify the P_b center,[11,12] the Si dangling bond at the Si(111)/SiO$_2$ interface, as the dominant point defect of the surface of porous silicon. Since its first observation at the (111) Si/SiO$_2$ interface of bulk samples the P_b center has become the object of detailed experimental[13-17] and theoretical[18,19] investigations. Due to the low spin number obtainable on mm^2 sized bulk samples the experimental studies were difficult and only under exceptional circumstances could the hyperfine interaction with the central ^{29}Si nucleus be resolved,[13] even though its angular dependence had not yet been determined. In the case of porous Si the large internal surface allows the EPR study of surface and interface defects under highly improved conditions. We will further show that the properties of the P_b defect can be used to characterize the internal surfaces of porous Si. Finally, thermal annealings at 400 °C under ultrahigh vacuum have been performed to determine the importance of hydrogen passivation of P_b centers in the as-grown samples.

EXPERIMENT

The porous layers were prepared from 2-in. diameter (100) oriented B-doped (10^{-2} Ω cm) Si wafers by electrochemical dissolution in a hydrofluoric acid electrolyte under currents varying between 20 and 50 mA/cm^2. Porosities were 45% and 80%; the layer thicknesses varied between 1 and 300 μm. Single samples of 4×8 mm^2 dimension were studied. The total surfaces of the layers has been estimated by a gas adsorption technique,[7,20] we obtain a value of 2×10^6 cm^2/cm^3, which corresponds to a total surface 200 times the external surface for 1-μm-thick samples of 45% porosity. The EPR measurements were performed in the 4–300 K temperature range with an X-band spectrometer in the absorption mode. Total impurity concentrations (O, H, C, F) were determined by nuclear reaction techniques.

EXPERIMENTAL RESULTS AND DISCUSSIONS

All as-grown samples yield under thermal equilibrium conditions between 4 and 300 K one dominant anisotropic EPR spectrum, which is shown in Fig. 1 (curves a–c) for the three orientations of the magnetic field parallel to the [110], [111], and [001] crystal directions. The spectrum is observed in the 45–300 K temperature range under slow adiabatic passage conditions and under rapid passage conditions giving rise to distorted line shapes at lower temperatures. For $T>45$ K the line shape is Lorentzian for $B\parallel[111]$. The peak to peak linewidths of the first derivative absorption spectrum vary between 1.2 G for $B\parallel[111]$ and 2.0 G for $B\parallel[110]$. The hyperfine interaction with one central Si nucleus is well resolved [Fig. 2 (curves a–c)]. In addition, nonresolved superhyperfine interaction is observed in the wings of the lines. From the angular variation of the resonances for a rotation of the magnetic field in the (110) plane (Fig. 3) the point symmetry of the defect, trigonal C_{3v}, and the principal values of the g tensor were determined:

$$g_1=2.0017\pm0.0003,\quad B\parallel[111]\ ,$$

$$g_2=2.0091\pm0.0003,\quad B\perp[111]\ ,$$

$$g_3=2.0091\pm0.0003,\quad B\perp[111]\ .$$

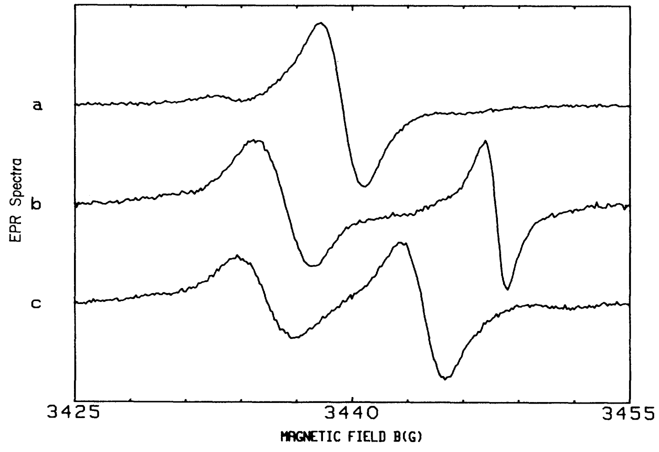

FIG. 1. EPR spectrum of a 10-mm^2 porous Si:B sample at $T=300$ K for three orientations of the magnetic field (a) $B\parallel[001]$; (b) $B2\parallel[111]$; (c) $B\parallel[110]$.

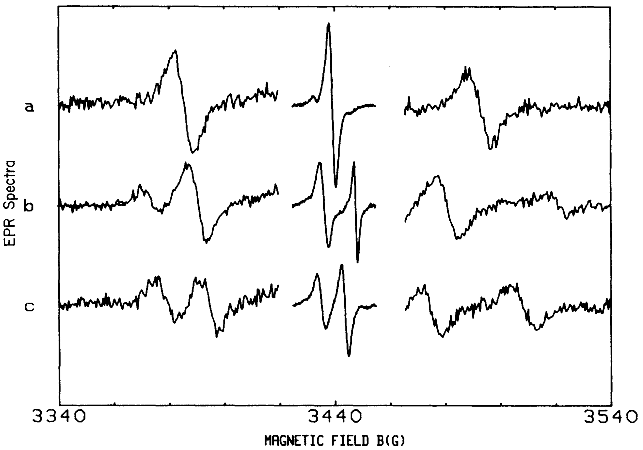

FIG. 2. EPR spectra at higher gain ($\times 25$) showing the central hyperfine structure for (a) $B\parallel[001]$, (b) $B\parallel[111]$, (c) $B\parallel[110]$; $T=300$ K.

The symmetry and the absolute values of the g tensor are identical to that of the (111) P_b center observed on bulk surfaces at low temperature ($T=18$ K);[15] they identify thus this defect as the neutral, singly charged Si dangling bond at the (111) surface. P_b centers on (111) surfaces can be distinguished from those on (100) surfaces:[21] the symmetry of the P_b centers (P_{b0}, P_{b1}) at the (100) surface is lower than trigonal and the principal values of the g tensor are different; this allows an identification of the surface geometry. The P_b centers observed in our samples are situated on (111) surfaces, which seems to indicate a preferential formation of (111) oxidized surfaces. Whereas in Si/SiO$_2$ interface studies on (111) surfaces of bulk materials only one of the four equivalent (111) dangling-bond defects, which is oriented perpendicular to the surface, is predominantly[15] observed, we observe here in porous Si simultaneously the four branches with the same intensity. This demonstrates that even though the formation of the pore structure from the (100) surface substrate is highly directional this does not lead to a preferential formation of any of the four equivalent (111) surfaces.

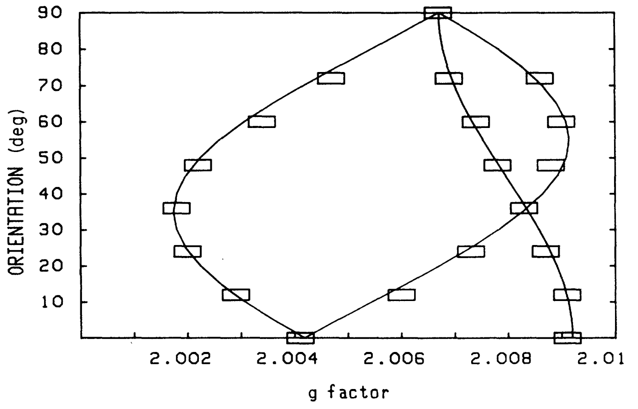

FIG. 3. Experimental (rectangle) and simulated (line) angular variation of the g tensor of the P_b center for a variation of the magnetic field in the (110) plane; $T=300$ K.

The P_b center is a very specific interface defect of the Si/SiO_2 interface and is not observed on nonoxidized surfaces; the fact that we observe this defect in porous Si allows us to conclude that a fraction of the surface of the porous Si samples is covered by a SiO_2 layer, even though these samples have not been purposely oxidized; these conclusions are in agreement with the oxygen content detected in these samples.[6] The concentration of $\approx 1\times 10^{15}$ cm^{-2} corresponds to a monolayer coverage, if the entire surface were oxidized. We come back to this point below, when discussing the absolute spin concentrations.

The excellent signal to noise ratio (> 100:1) of the EPR spectra of the P_b centers allowed the further resolution of the central Si hyperfine interaction of this defect (Fig. 2); as in the case of the EPR studies of the P_b center on bulk samples[13] the linewidth of the hyperfine lines is higher ($\approx$6 G) as compared to the one for the $I=0$ transition (1.2–2.0 G). The full angular variation of the hyperfine interaction (Fig. 4) has been measured for the first time; the results show the hyperfine-interaction tensor to be of trigonal symmetry; equal intensities are found for the four (111) equivalent resonances; we have determined the principal values of the hyperfine tensor (see Table I). The principal values of hyperfine tensor A_1, A_2, A_3 determined by us are slightly different from the previously reported values;[13] this might be due to either the different temperatures at which these measurements were done or the more precise orientation possible in our case, where one single sample is measured, as compared to the stack of samples used in Ref. 13. Severe line-shape distortion due to rapid passage conditions did not allow us a sufficiently precise determination of the A tensor at $T=18$ K in the porous samples to conclude this question. From our results we can determine the "s" and "p" densities of the electron wave function and the degree of localization of the electron in the dangling-bond orbital on the central Si atom: where a and b are defined as usual by $a=(A_\parallel+2A_\perp)/3$ and $b=(A_\parallel=A_\perp)/3$ (see Table II). For a pure sp^3 dangling-bond defect an s/p ratio of 0.25 would be expected, which indicates a tendency towards planar sp^2 hybridization of this defect at the (111) surface.

TABLE I. Principal values of the hyperfine tensor in units of 10^{-4} cm^{-1}.

	This work (300 K)	Ref. 13 (18 K)
$A_1 \parallel [111]$	139±3	146±5
$A_2 \perp [111]$	73±3	85±5
$A_3 \perp [111]$	73±3	85±5

The concentration of the neutral P_b defect was measured by comparison with a ruby spin standard sample. The values quoted below are referred to the total internal surface of the porous Si, which for 45% porosity 1-μm-thick sample has been estimated to be 200 times the external surface.[20] A typical value for as-grown samples aged by exposure to air for some weeks is $[P_b]=4\times 10^9$ cm^{-2}, which is an unreasonably small spin density given the poor interface quality expected in these naturally oxidized samples. From P_b-center studies on Si/SiO_2 interfaces on bulk samples defect concentrations between 10^9 and 10^{13} cm^{-2} have been reported, the lowest value corresponding to state-of-the-art interfaces. From this we would expect only a small fraction of the total surface to be oxidized. However, as the nuclear reaction analysis of our samples had shown a high degree of hydrogen contamination with a [H] to [Si] ratio of 0.1 we expected that most of the P_b centers were passivated by H and that the real P_b-center concentration was significantly higher. To test this possibility, we have annealed as-prepared samples at 400 °C in ultrahigh vacuum for 30 min, a temperature where H is known to outdiffuse.[6] And indeed, the annealing increased the neutral P_b-center concentration in our samples by a factor of $\approx$70, corresponding now to surface concentrations of 3×10^{11} cm^{-2} assuming that the entire internal surface is composed of (111) oxidized Si surfaces. If we knew the surface density of the P_b

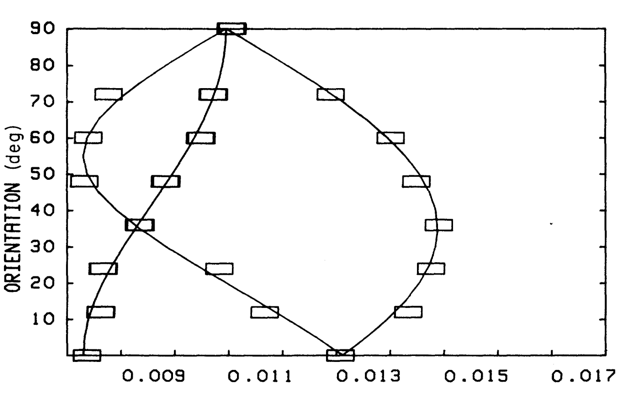

FIG. 4. Experimental (rectangle) and simulated (line) angular variation of the central hyperfine tensor of the P_b center for a variation of the magnetic field in the (110) plane; $T=300$ K.

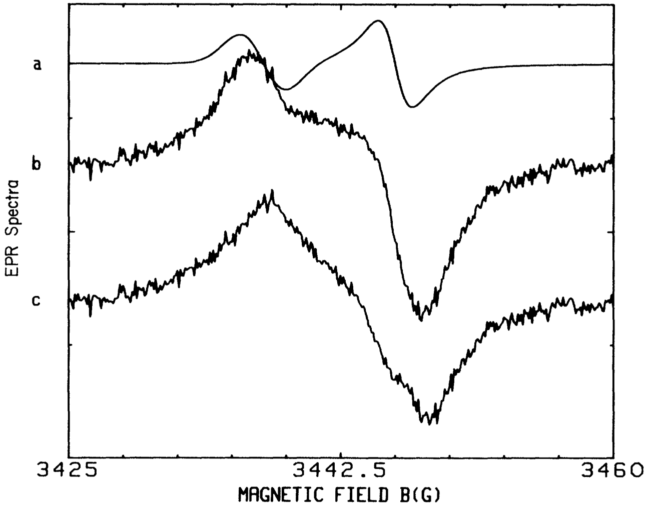

FIG. 5. EPR spectrum of an 80%-porosity sample showing (b) the experimental spectrum and its decomposition into (a) the P_b center and (c) the $g=2.0055$ dangling-bond defect of amorphous Si.

TABLE II. Hyperfine coupling constants (a,b), s and p spin densities, and the total spin density on the central Si nucleus of the P_b centers in porous Si and on bulk Si.

	a (10^{-4} cm^{-1})	b (10^{-4} cm^{-1})	"s" density	"p" density	s/p ratio	Total density
P_b (por)	95	22	0.07	0.65	0.11	0.72
P_b (bulk) (Ref. 13)	105.3	20.3	0.076	0.60	0.13	0.68
Calc. pure "s","p" state (Ref. 22)	1380	33.7				

center the fraction of the oxidized surface could be estimated. This information is given by the peak-to-peak linewidth of the P_b-center resonance for B$\|$[111], which has been shown to be a measure of the spin concentration due to a concentration-dependent dipolar broadening.[23] The linewidth has been shown to vary from 1.2 G for defect concentrations of $\approx 10^{11}$ cm^{-2} up to 2.0 G for concentrations of 2×10^{12} cm^{-2}. In our case we observe for both as-grown and 400 °C annealed samples a linewidth of 1.2 G, which determines the defect concentrations to $\leq 10^{11}$ cm^{-2}. Such a concentration requires that the fraction of the internal surface, covered by an oxide layer, must be of the order of 0.5. This estimation is in agreement with the NRA results: in freshly prepared layers 10–20 % of the pore surface is oxidized but aging of a few days under ambient conditions increases the oxygen context by 5 and decreases the H content by a factor of 3.

The orientational dependency of the P_b center, reflecting the symmetry of the monocrystalline substrate, demonstrate further the monocrystalline character of the porous Si surfaces, even in high-porosity (80%) samples. Whereas no indication for the presence of amorphous Si inclusions, which can be identified by the different paramagnetic defects, typical for such material, has been found after thermal annealing in 45%-porosity samples, this is not the case in the 80%-porosity material. Here both perfectly oriented P_b centers and amorphous Si inclusions are observed simultaneously. The EPR spectrum of the 80%-porosity thermally annealed samples is a superposition of two different spectra: the anisotropic P_b-center spectrum and an isotropic line of 8-G peak-to-peak linewidth and a g factor of $g=2.0055$ (Fig. 5). The decomposition of the spectrum (curve b, total spectrum; a, simulated P_b-center spectrum; c, difference spectrum) is confirmed by an analysis of the central hyperfine-interaction spectrum of the P_b center, which could also be resolved in this case. The isotropic signal is attributed from its EPR parameters to the neutral dangling-bond defect in amorphous Si.

CONCLUSION

Our EPR results demonstrate that the neutral (111) dangling-bond defect, P_b, is the main paramagnetic defect with concentrations in the 10^{11} cm^{-2} range in p^+ porous silicon, which has been exposed to ambient conditions. The angular variation of the hyperfine interaction with the central ^{29}Si nucleus has been determined. The surface of porous Si is monocrystalline with a preferential (111) geometry of the oxidized surfaces. A high fraction (0.5) of the surface is oxidized. The P_b defect is a recombination center, the presence of which is expected to be detrimental to radiative recombination processes. The depassivation of the P_b center by 400 °C vacuum annealing will strongly reduce the photoluminescence efficiency. In order to obtain high radiative efficiencies oxide layers of high interface quality have to be grown to replace the oxide formed by aging under ambient conditions and/or passivation of the P_b centers must be achieved. Whereas no indication of amorphous Si were found in 45%-porosity samples such inclusions are observed in 80%-porosity photoluminescent samples after 400 °C thermal annealing

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