

## Hydrogen passivation of carbon $P_b$ like centers at the 3C- and 4H-SiC/SiO<sub>2</sub> interfaces in oxidized porous SiC

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The effect of forming gas and vacuum annealing on the concentration of carbon dangling bond ( $P_{bc}$ ) centers at 3C- and 4H-SiC/SiO<sub>2</sub> interfaces has been studied by electron paramagnetic resonance (EPR) spectroscopy. Our results show efficient passivation at 400 °C and depassivation for temperatures above 850 °C. A dissociation energy of  $(4.3 \pm 0.3)$  eV has been determined for both polytypes. © 2006 American Institute of Physics. [DOI: 10.1063/1.2179128]

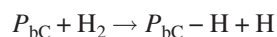
The large density ( $>10^{13}$  cm<sup>-2</sup>) of electrically active interface traps with levels close to the conduction and valence band edges is a limiting factor for the performance of SiC/SiO<sub>2</sub> metal oxide semiconductor devices.<sup>1</sup> These traps located at or near the interface between the SiC substrate and the oxide layer were tentatively attributed to residual carbon clusters or to interfacial suboxides.<sup>2-4</sup> In addition carbon and silicon dangling bond defects related to the structural mismatch between the crystalline SiC and the amorphous SiO<sub>2</sub> layer are also expected to be present and electrically active. These defects are analogous to the  $P_b$  centers of the Si/SiO<sub>2</sub> interface. In recent EPR studies<sup>5-8</sup> the carbon dangling bond center—labelled  $P_{bc}$ —has been assessed as the main paramagnetic interface defect at the SiC/SiO<sub>2</sub> interface. From photo electron paramagnetic resonance (EPR) it has been deduced that this defect is a deep trap with an optical ionization energy of 1.8 eV. From previous studies of Pb centers in Si/SiO<sub>2</sub> it is well known that such centers can be passivated by low temperature (400 °C) forming gas annealing.<sup>9-12</sup> In the case of SiC/SiO<sub>2</sub> forming gas treatments have also been attempted to reduce the shallow trap densities. In these studies, the conditions known to work well for the Si/SiO<sub>2</sub> interface defects have generally been used as a guide and annealing in forming gas, pure hydrogen<sup>13</sup> and nitrous oxide NO (Ref. 14) were attempted. But surprisingly no significant reduction of the shallow interface trap density was observed.

It thus seemed interesting to investigate by EPR whether the  $P_{bc}$  center at the SiC/SiO<sub>2</sub> interface can be passivated or not, and compare the results to those obtained for silicon Pb centers at the Si/SiO<sub>2</sub> interface. To overcome the difficulties in the observation of these interface defects in bulk SiC/SiO<sub>2</sub> samples we have used monocrystalline oxidized porous SiC samples for this study. Taking advantage of the highly increased surface area in porous SiC substrates, we have recently been able to identify by EPR the carbon dangling bond center at the 6H-4H-, and 3C-SiC/SiO<sub>2</sub> interfaces.<sup>5-8</sup> We named this defect for obvious reasons the  $P_{bc}$  center. The  $P_{bc}$  center is structurally similar to the  $P_{b0}$  center at the Si/SiO<sub>2</sub> interface; it consists of a C atom bonded to three Si atoms of the SiC crystal with one dan-

gling bond directed to the oxide. We report here the effect of hydrogen and subsequent vacuum annealing on the  $P_{bc}$  defect at the 3C and 4H SiC/SiO<sub>2</sub> interfaces.

Porous samples were obtained by electrochemical dissolution of *n*-type 4H (0001) and 3C (001) SiC substrates. For details of the dissolution parameters and the related pore structures, see Refs. 15 and 16. For the EPR experiments we prepared samples of 4H-SiC triangular morphology 20 μm thick followed by dendritic morphology of about 90 μm thickness. In the case of the cubic SiC the morphology was triangular and the thickness of the samples was about 130 μm. Samples were oriented along high symmetry directions. The estimated increase in the surface area as compared to the external surface is  $>1000$ . The samples were then thermally oxidized in dry oxygen at a pressure of 35 mbar in a quartz furnace. The oxidation was carried out in two steps: a first low temperature oxidation was performed at 300 °C for 1 h, followed by a high temperature oxidation at 1000 °C for 10 min. The samples were subsequently annealed at 400 °C in a forming gas (5% H<sub>2</sub>, 95% N<sub>2</sub>) atmosphere (650 mbar) for 2 or 48 h. After this passivation treatment, some samples were further treated by a vacuum anneal (residual pressure  $<4 \times 10^{-7}$  mbar) at temperatures ranging from 600 to 1000 °C. The EPR experiments were performed at an X-band frequency (9.6 GHz) at 300 K; the angular variations of the EPR spectra for a rotation of the magnetic field in the (110) plane for 3C-SiC and the (1100) plane for 4H-SiC were studied. The  $P_{bc}$  density was determined by a numerical double integration of the  $P_{bc}$  center spectrum.

After the thermal oxidation of the 3C and 4H SiC samples, we observed the anisotropic spectrum of the  $P_{bc}$  defects previously reported<sup>5-8</sup> [Fig. 1(a)]. In the 3C polytype the trigonal symmetry of the defect gives rise for the particular magnetic field orientation  $B \parallel [001]$  to a single line EPR spectrum, whereas the equivalent defect in 4H-SiC gives rise to a two line spectrum for  $B \parallel c$ . After an anneal in forming gas at 400 °C for 3 h the intensity of the  $P_{bc}$  spectrum is reduced by a factor of 20 [Fig. 1(b)] for both polytypes. In the following we will assume, in analogy to the case of the  $P_{b0}$  center at the Si/SiO<sub>2</sub> interface, that the decrease of the  $P_{bc}$  center corresponds to the formation of a C–H hydrogen bond,



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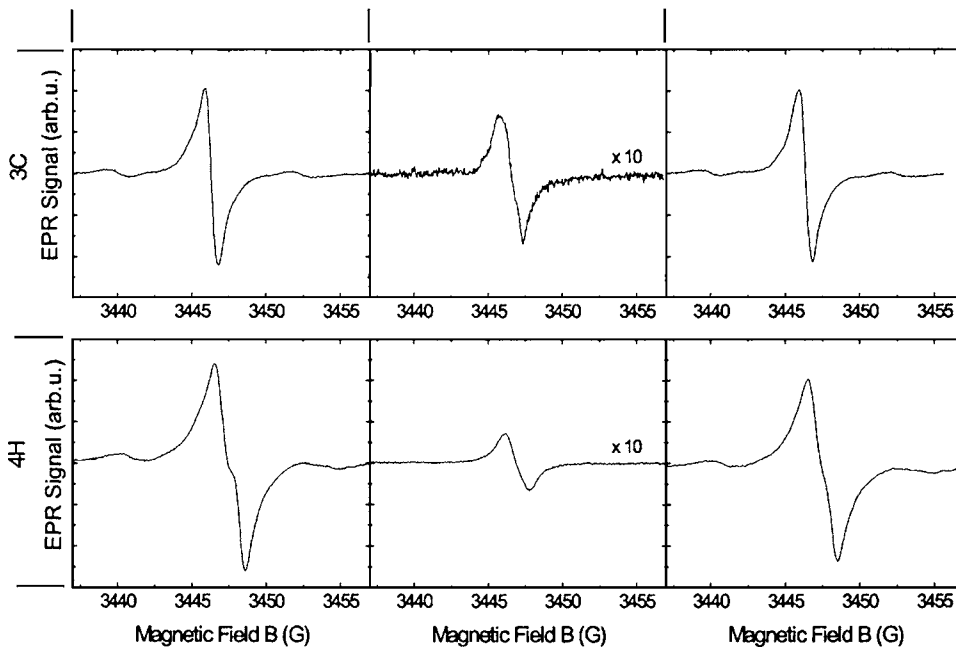


FIG. 1. EPR spectra of 3C-SiC/SiO<sub>2</sub> (upper panel) and 4H-SiC/SiO<sub>2</sub> (lower panel) measured at room temperature for  $B\parallel[001]$ ,  $B\parallel c$  in the as-oxidized state (a), after forming gas annealing (b) and after vacuum annealing at 950 °C (1 h) (c); in (b) gain is multiplied by 10.

To verify this model we also investigated the reverse reaction, depassivation by vacuum annealing at different temperatures. As shown in Fig. 1(c) we can effectively depassivate the  $P_{bc}$ -H centers in both 3C and 4H polytypes but only at temperatures substantially higher than those required for the  $P_{b0}$  center. We have investigated the dissociation process in more detail by performing isochronal (1 h) vacuum annealing at temperatures between 600 °C and 1000 °C. Figure 2 presents the evolution of the relative defect density as a function of annealing temperatures. We observe that the dissociation reaction occurs at temperature above 800 °C for the 3C- and 4H-SiC samples. We can model the depassivation process by assuming that the rate of change of the defect density is proportional to the concentration of passivated centers [ $P_{bc}$ -H]. This leads to the following first order differential equation characterized by a rate constant  $k_d$ :

$$\frac{d[P_{bc}]}{dt} = k_d[P_{bc} - H].$$

We have determined the temperature dependence of  $k_d$ . Figure 3 shows that, within the experimental error,  $k_d$  follows a

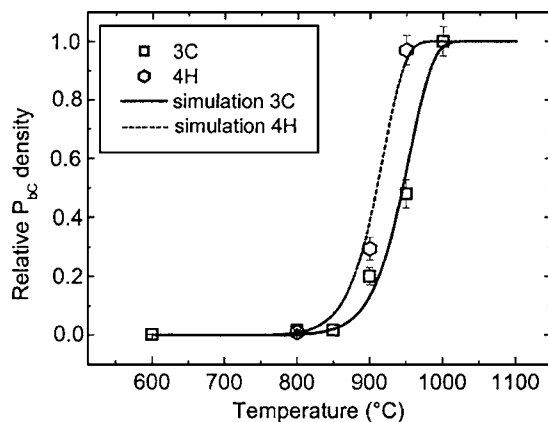


FIG. 2. Relative  $P_{bc}$  defect density at the 3C- and 4H-SiC/SiO<sub>2</sub> interfaces (squares and hexagons, respectively) as a function of annealing temperature for vacuum annealing of 1 h. The solid lines represent the fits according to the proposed model (parameters are given in the text).

simple Arrhenius behavior with  $k_d = k_0 \exp(-E_d/kT)$ , where  $k$  is the Boltzmann constant and  $k_0$  and  $E_d$  are, respectively, the pre-exponential factor and the dissociation energy. From a least square fit, we obtain the following numerical values:  $k_0 = 1.5 \times 10^{14} \text{ s}^{-1}$  and  $3 \times 10^{14} \text{ s}^{-1}$  for the 3C and 4H polytypes, respectively, and for both polytypes, a similar dissociation energy  $E_d$  of 4.3 eV with a standard error of  $\pm 0.3$  eV.

In Table I we compare these dissociation energies to the ones of the silicon  $P_b$  centers at the (111)Si/SiO<sub>2</sub> and (001)Si/SiO<sub>2</sub> interfaces. We note that the dissociation energies of the Si dangling bonds are significantly lower than the value we have determined for the  $P_{bc}$  center. This is not surprising as the C-H bond is known to be stronger than the Si-H bond.

We can also compare our results with the previous EPR studies on bulk SiC/SiO<sub>2</sub> structures.<sup>20,21</sup> In these studies paramagnetic centers have been observed after high temperature annealing of oxidized samples but it was not possible to relate them to  $P_b$  like interface defects. The difficulty arose from the low signal to noise ratios impeding the observation of any hyperfine structure and the higher linewidth of the EPR spectra rendering the spectra apparently isotropic. As an isotropic  $g$ -factor does not fit with the expected properties for  $P_b$  centers—trigonal or lower symmetries as expected—

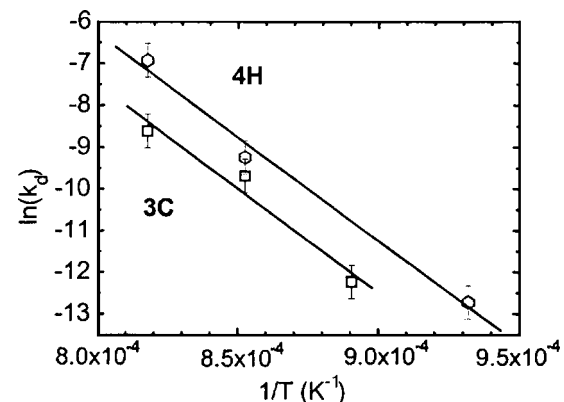


FIG. 3. Arrhenius plots of the rate constants  $k_d$  for the 3C and 4H polytypes.

TABLE I. Dissociation energies of carbon  $P_{bc}$  centers in SiC/SiO<sub>2</sub> and silicon  $P_b$  centers in Si/SiO<sub>2</sub>, respectively, at different interferences. The dissociation energy of the “heat treatment center” is also listed.

Interface	Defect	Dissociation energy (eV)	Reference
(111)Si/SiO <sub>2</sub>	$P_b$ (Si)	2.90±0.05	17
		2.83±0.03	12
		2.78±0.02	18
		2.56±0.06	10
		2.60±0.06	19
(001)Si/SiO <sub>2</sub>	$P_{b0}$ (Si)	2.86±0.04	18
(001)Si/SiO <sub>2</sub>	$P_{b1}$ (Si)	2.91±0.03	18
3C-SiC/SiO <sub>2</sub>	C related		
6H-SiC/SiO <sub>2</sub>	center	4.0±0.3	20 and 21
3C-SiC/SiO <sub>2</sub>	$P_{bc}$ (C)	4.3±0.3	
4H-SiC/SiO <sub>2</sub>		4.3±0.3	this work

MacFarlane *et al.* attributed the centers to “heat treatment centers” without any specific microscopic model. They have also studied the effects of forming gas annealing on these heat treatment centers; their results are included in Table I. We see that the dissociation energies of the  $P_{bc}$  centers determined in our work compare well with the activation energies previously determined for the thermal defect in 3C- and 6H-SiC/SiO<sub>2</sub>. In their study the higher dissociation energies of the thermal defects as compared to Si  $P_b$  centers at the Si/SiO<sub>2</sub> interfaces were used as the main argument to attribute these defects to carbon dangling bond defects. In view of the now available results on the weak  $g$ -tensor anisotropies<sup>5–8</sup> and the identical forming gas behavior, it is clear that the defects observed in their study on bulk samples and in our studies of oxidized porous samples are, in fact, identical.

In conclusion, we have demonstrated that the carbon dangling bond  $P_{bc}$  center at the SiC/SiO<sub>2</sub> interface can be efficiently passivated by low temperature (400 °C) forming gas annealing. The depassivation process was studied and the dissociation energies were determined. The higher thermal stability of the passivation of the carbon  $P_{bc}$  center should be

of interest for SiC MOSFET processing. As the  $P_{bc}$  center is a deep defect its passivation will not modify the shallow trap density generally monitored in electrical measurements.

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- <sup>1</sup>N. S. Saks, S. S. Mani, and A. K. Agarwal, Appl. Phys. Lett. **76**, 2250 (2000).
- <sup>2</sup>W. Lu, L. C. Feldman, Y. Song, S. Dhar, W. E. Collins, W. C. Mitchel, and J. R. Williams, Appl. Phys. Lett. **85**, 3495 (2004).
- <sup>3</sup>S. Dhar, L. C. Feldman, K. C. Chang, Y. Cao, L. M. Porter, J. Bentley, and J. R. Williams, J. Appl. Phys. **97**, 074902 (2005).
- <sup>4</sup>E. Pippel, J. Woltersdorf, H. O. Olafson, and E. O. Sveinbjornsson, J. Appl. Phys. **97**, 034302 (2005).
- <sup>5</sup>H. J. von Bardeleben, J. L. Cantin, M. Mynbaeva, S. E. Saddow, Y. Shiskin, R. P. Devaty, and W. J. Choyke, in “Silicon Nitride and Silicon Dioxide Thin Insulating Films VII”, *Electrochemical Society Proceedings. 2003-2*, edited by R. E. Sah, M. J. Deen, D. Landheer, K. B. Sundaram, W. D. Brown, and D. Misra, 39 (The Electrochemical Society, Inc., 2003).
- <sup>6</sup>J. L. Cantin, H. J. von Bardeleben, Y. Ke, Y. Shiskin, R. P. Devaty, and W. J. Choyke, Phys. Rev. Lett. **92**, 015502 (2004).
- <sup>7</sup>H. J. von Bardeleben, J. L. Cantin, Y. Shiskin, R. P. Devaty, and W. J. Choyke, Mater. Sci. Forum **457–460**, 1457 (2004).
- <sup>8</sup>H. J. von Bardeleben, J. L. Cantin, Y. Ke, Y. Shiskin, R. P. Devaty, and W. J. Choyke, Mater. Sci. Forum **483–485**, 273 (2005).
- <sup>9</sup>K. L. Brower, Phys. Rev. B **38**, 9657 (1988).
- <sup>10</sup>K. L. Brower, Phys. Rev. B **42**, 3444 (1990).
- <sup>11</sup>A. Stesmans, Appl. Phys. Lett. **68**, 2076 (1996); **68**, 2723 (1996).
- <sup>12</sup>A. Stesmans, J. Appl. Phys. **92**, 1317 (2002).
- <sup>13</sup>K. Fukuda, W. J. Cho, K. Arai, S. Suzuki, J. Senaki, and T. Tanaka, Appl. Phys. Lett. **77**, 866 (2000).
- <sup>14</sup>G. Y. Chung, J. R. Williams, K. Mc Donald, and L. C. Feldman, J. Phys.: Condens. Matter **16**, S1857 (2004).
- <sup>15</sup>Y. Shiskin, W. J. Choyke, and R. P. Devaty, Mater. Sci. Forum **457–460**, 1467 (2004).
- <sup>16</sup>Y. Shiskin, Y. Ke, R. P. Devaty, and W. J. Choyke, Mater. Sci. Forum **483–485**, 251 (2005).
- <sup>17</sup>A. R. Wilkinson and R. G. Elliman, Phys. Rev. B **68**, 155302 (2003).
- <sup>18</sup>J. H. Stathis, J. Appl. Phys. **77**, 6205 (1995).
- <sup>19</sup>R. Khatri, P. Asoka-Kumar, B. Nielsen, L. O. Roellig, and K. G. Lynn, Appl. Phys. Lett. **65**, 330 (1994).
- <sup>20</sup>P. J. Mac Farlane and M. E. Zvanut, J. Electron. Mater. **28**, 144 (1998).
- <sup>21</sup>P. J. Mac Farlane and M. E. Zvanut, J. Appl. Phys. **88**, 4122 (2000).