## Temperature dependence of chemical-vapor deposition of pure boron layers from diborane

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Surface reaction mechanisms are investigated to determine the activation energies of pure boron (PureB) layer deposition at temperatures from  $350 \,^{\circ}$ C to  $850 \,^{\circ}$ C when using chemical-vapor deposition from diborane in a commercial Si/SiGe epitaxial reactor with either hydrogen or nitrogen as carrier gas. Three distinguishable regions are identified to be related to the dominance of specific chemical reaction mechanisms. Activation energies in H<sub>2</sub> are found to be 28 kcal/mol below 400 °C and 6.5 kcal/mol from 400 °C to 700 °C. In N<sub>2</sub>, the value decreases to 2.1 kcal/mol for all temperatures below 700 °C. The rate of hydrogen desorption is decisive for this behavior. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4752109]

Pure boron (PureB) layer depositions have in recent years been applied for creating the p<sup>+</sup>-region of extremely shallow, less than 10-nm deep, silicon  $p^+n$  junction diodes for a number of leading-edge device applications.<sup>1</sup> Particularly impressive performance has been achieved for the application to bulk-Si photodiodes for detecting low penetration-depth beams.<sup>2–5</sup> Ideal diode characteristics have been achieved for deposition temperatures in the 400 °C-700 °C range. The option of depositing at temperatures below  $\sim 500$  °C, which together with the fact that the deposition is conformal and highly selective to Si, makes PureB technology highly compatible with amorphous-/polysilicon-/ crystalline-silicon thin-film device processing. Moreover, these properties also make it an attractive process for creating junctions on silicon nanowires and advanced CMOS (complementary metal-oxide-semiconductor) transistors including source/drain in p-type FinFETs.<sup>6,7</sup> These applications require a sub-3-nm thick layer to avoid excess series resistance through the high-resistivity PureB layer.

In the present work, the deposition is performed in a commercial Si/SiGe epitaxial reactor by exposing the Si surface to diborane ( $B_2H_6$ ). At 700 °C, in the first few seconds of exposure, the boron atoms interact with the Si surface sites to quickly build up something like an atomic layer plane, and upon further deposition, the boron coverage readily exceeds one monolayer (1 ML). After this, the boron atoms will be deposited on a full PureB surface, which is a process that has a much slower, well-controlled deposition rate. In the past, it has been shown that less than 2-nm-thick layers can be deposited with good reliability and uniformity by a suitable adjustment of deposition parameters such as deposition time, temperature, partial pressures, and flow rates.<sup>8</sup>

In this paper, an investigation is presented of the surface reaction mechanisms and activation energies of PureB layer deposition in the temperature range of 350 °C to 850 °C. At the lower temperatures, the carrier gas has a large influence on the ability to create the first full boron coverage of the Si. Nevertheless, by first creating a full PureB coverage at 700 °C, which is smooth and uniform, and then proceeding with the low-temperature depositions, the boron-on-boron activation energies could be determined over the whole temperature range. The deposition behavior is also studied for a carrier gas of either H<sub>2</sub> or N<sub>2</sub>. The latter can be considered to be an inert gas below about 800 °C. In a parallel paper,<sup>9</sup> the experimental data are presented here and the derived activation energies have been applied as input for an analytical kinetic model developed to describe the deposition kinetics and the deposition chamber characteristics that determine the deposition rates of PureB-layers on a nonrotating silicon wafer. The model takes into consideration the diffusion mechanism of the diborane species through the stationary boundary layer over the wafer, the gas phase processes, and the related surface reactions by applying the actual parabolic gas velocity and temperature gradient profiles in the reactor.

The overall chemical reaction describing the diborane deposition is quite simple and given by

$$B_2H_6(g) \to 2B(s) + 3H_2(g),$$
 (R1)

where (g) indicates the gas phase and (s) the solid phase. However, the individual reactions leading to this final result are quite complicated.

Several studies have been published on reactions between B hydrides and either Si(100) or boron surfaces.<sup>11–14</sup> The possible gas-phase chemical reactions are very complex and include the formation of several high-order boranes (B<sub>3</sub>H<sub>7</sub>, B<sub>4</sub>H<sub>10</sub>, and B<sub>5</sub>H<sub>11</sub>). The work of Fehlner *et al.*,<sup>15–18</sup> Baylis *et al.*,<sup>19</sup> and Mappes *et al.*<sup>20</sup> specifically investigated the formation of solid boron from diborane and concluded that the dominant boron hydride gas-phase species is BH<sub>3</sub>. Modeling studies of the intentional doping of Si thin films, using B<sub>2</sub>H<sub>6</sub> as a dopant source gas, have also indicated that the primary gas-phase reaction pathways are the decomposition of B<sub>2</sub>H<sub>6</sub> to BH<sub>3</sub> and the subsequent recombination to again form B<sub>2</sub>H<sub>6</sub>,<sup>21–25</sup> as shown in reaction (R2). This assumption is also supported by computational studies that have shown that the

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unimolecular decomposition and recombination reactions are the energetically favorable reaction pathways<sup>24,26</sup>

$$B_2H_6(g) \to 2BH_3(g). \tag{R2}$$

As Sarubbi et al.<sup>7</sup> mentioned, in the first seconds of exposure to diborane, boron atoms deposit via interaction with silicon surface sites and the coverage of the deposited layer can grow to exceed 1 ML. After this stage, the boron atoms will be deposited on a closed PureB surface. At each stage of the deposition, the silicon and/or boron surfaces have many dangling bonds, some of which will be terminated with hydrogen atoms. When BH<sub>3</sub> molecules interact with these bonds, there are several possible reactions. With one precursor involved and four types of surface sites, H-terminated Si/B sites, and H-free Si/B sites, there are four heterogeneous reactions that must be considered. The most probable reactions, from the point of view of thermodynamics and kinetics, are listed in Table I. In the notation, e.g., H\_Si/H\_B are the silicon/boron atoms with H-terminated dangling bonds, and  $\circ Si/\circ B$  are the silicon/boron atoms with free dangling bonds. These are the most probable reactions which are supported by silicon doping studies which have indicated that BH<sub>3</sub> is the active gas species that initially adsorbs on an open surface sites:<sup>21–25</sup> the BH<sub>3</sub> molecule will impinge upon the growth surface (Si/PureB) and form an activated BH2site complex.

The released atomic hydrogen in reactions (R3) and (R5) reacts *in-situ* with the H-terminated Si/B surface sites with the following possible surface reactions:<sup>27,28</sup>

$$H(g) + H_Si(s) \overleftrightarrow{} H_2(g) + \circ Si(s), \tag{R7}$$

$$\mathbf{H}(\mathbf{g}) + \mathbf{H}_{\mathbf{B}}(\mathbf{s}) \overleftarrow{\rightarrow} \mathbf{H}_{2}(\mathbf{g}) + \circ \mathbf{B}(\mathbf{s}). \tag{R8}$$

The forward direction of these two reactions (R7) and (R8) releases the hydrogen from the surface and decreases the H surface coverage. The presence of hydrogen gas can suppress this reaction. The reverse direction describes the reaction of molecular hydrogen with the surface. These two processes are illustrated in Fig. 1.

In the deposited layer, there are some possible cross-linked reactions<sup>29,30</sup> between two adjacent Si-H and B-H bonds (Fig. 1)

$$H_Si(s) + H_Si(s) \stackrel{\leftarrow}{\rightarrow} Si_Si(s) + H_2(g),$$
 (R9)

$$H_B(s) + H_B(s) \xrightarrow{\leftarrow} B_B(s) + H_2(g),$$
 (R10)

$$H_B(s) + H_Si(s) \stackrel{\leftarrow}{\rightarrow} B_Si(s) + H_2(g).$$
(R11)

TABLE I. Possible heterogeneous reactions involved in PureB-layer deposition with a  $B_2H_6$  precursor.

Reaction no.	$BH_3$ reaction with	Reaction
(R3)	Free Si surface sites	$BH_3(g) + \circ Si(s) \rightarrow H_2B\_Si(s) + H(g)$
(R4)	H-terminated Si sites	$BH_3(g) + H\_Si(s) \rightarrow H_2B\_Si(s) + H_2(g)$
(R5)	Free B surface sites	$BH_3(g) + \circ B(s) \rightarrow H_2B\_B(s) + H(g)$
(R6)	H-terminated B sites	$BH_3(g) + H_B(s) \rightarrow H_2B_B(s) + H_2(g)$



FIG. 1. Some of the possible secondary reactions when a Si surface is exposed to  $\mathrm{B}_2\mathrm{H}_6.$ 

In addition, there are a few other possible reactions like migration of the attached boron atoms along the surface (e.g., migration of deposited boron atoms along a boron-covered surface, (R12) and (R13)) and/or boron diffusion into the silicon substrate as a dopant (R14) (see Fig. 1)

$$H_2B\_B(s) + \circ B(s) \to \circ B(s) + H_2B\_B(s), \quad (R12)$$

$$H_2B\_B(s) + \circ B(s) \to \circ B(s) + H_2B\_B(s),$$
(R13)

$$Si_B(s) \rightarrow \circ Si(s) + B$$
 (diffused). (R14)

Theoretically, the above nine reactions (reactions (R3)-(R11)) are all reversible. However, the diborane is thermodynamically unstable,<sup>15,19</sup> while the deposited PureB layer is stable. This is confirmed by an experiment where the PureB was deposited at 700 °C on a bare wafer and left in a H<sub>2</sub> atmosphere for time intervals varying from a couple of hours to several days. The PureB-layer thickness was monitored and there was no significant change over time. This means that in the temperature range 400 °C to 700 °C, no etching and/or desorption reaction of the deposited layer with H2 is to be expected. Therefore, the reverse direction of reactions (R3)–(R6) can be neglected, while reactions (R7) and (R8) must be taken into account. For reactions (R4) and (R6), two Si-H/B-H bonds must be broken, while this is only one Si-H/ B-H bond for reactions (R3) and (R5), respectively. Thus, the activation energies of reactions (R4) and (R6) must be higher than those of reactions (R3) and (R5), so that

$$E_{a}^{[R4]} > E_{a}^{[R3]}$$

and

$$E_a^{[R6]} > E_a^{[R5]}.$$

Assuming that the lowest energy path will dominate, boron deposition on either silicon or boron surfaces will be governed largely by the reactions (R3) or (R5), respectively.

Applying the same reasoning to reactions (R7)–(R10) gives

$$E_{a}^{[R9]} > E_{a}^{[R7]}$$

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$$E_a^{[R10]} > E_a^{[R8]}.$$

Furthermore, we assume that the surface bonded hydrogen atoms are swept away by reactions (R7) and (R8) for silicon/

boron surfaces, respectively, unless there are not enough free hydrogen atoms. This could be the case because the deposition of one  $BH_3$  molecule produces two surface-bonded hydrogen atoms but only one free hydrogen atom (reactions (R3) and (R5)).

The experiments were carried out in the ASM Epsilon 2000 Si/SiGe epitaxial reactor. The reactor has a large SiC susceptor, which it heated up to the deposition temperature by a crossed array of lamps above and below of the deposition chamber. The readout and control of the temperature is performed by one master thermo-couple at the center and three slaves at the front, rear, and side of the susceptor that were found to be constant to within  $\pm 0.5$  °C. Pure H<sub>2</sub> or N<sub>2</sub> was used as a carrier gas with a water and oxygen content below the ppm level and a total flow rate of 20 slm (standard liters per minute). For deposition of the PureB layer, diborane gas was used with several different input partial pressures. The diborane is diluted in H<sub>2</sub> but for the experiments with  $N_2$  as carrier gas, this  $H_2$  is less than 2% of the main gas flow. All experiments were performed at atmospheric pressure. Bare Si (100) 100 mm wafers with a thickness of 500–550  $\mu$ m were used. Before loading into the reactor, samples were immersed in a diluted HF (0.55%) solution for 4 min to remove native oxide and H-passivate the surface. This was followed by Marangoni drying. In the deposition chamber, a 4 min H-bake was performed. The layer thickness was measured in-line using ellipsometry which has an acceptable accuracy and good repeatability for smooth layers.<sup>10</sup> To obtain smooth layers in all cases where the boron-on-boron deposition rate is to be determined, the initial deposition is performed at 700 °C, at which temperature complete (monolayer) B coverage of the Si is readily achieved.' Subsequently, a series of thicker layers are deposited at the temperature to be investigated. The sheet resistance of some of the PureB layers was determined by using the method described by Sarubbi et al."

In Fig. 2, Arrhenius plots of the deposition rate (DR) of the PureB layers is shown for two different diborane partial pressures  $P_{high}$  and  $P_{low}$  that are 3.39 and 1.7 mTorr, respectively. For H<sub>2</sub> carrier gas and the high partial pressure, three linear regions are clearly discerned, while for low partial



FIG. 2. Deposition rate of PureB layers on B-covered Si as a function of temperature for different diborane partial pressures ( $P_{high} = 3.39 \, \text{mTorr}$ ,  $P_{low} = 1.7 \, \text{mTorr}$ ) and a carrier gas of either  $H_2$  or  $N_2$ . The values are an average of 21 measurements taken over each wafer. The extracted activation energies in the linear regions are indicated.

pressure, only two regions are seen. In the latter case, for temperatures below approximately 400 °C, there is no measurable deposition. In the case of  $N_2$  carrier gas with the high diborane partial pressure, the curve shows two linear regions, one below and the other above 700 °C.

In each linear region of the curves in Fig. 2, the deposition rate can be expressed by the Arrhenius equation

$$DR(T) = Aexp\left(\frac{-E_a}{RT}\right),$$
(1)

where A,  $E_a$ , R, and T are the frequency factor, activation energy, gas constant of the substrate, and deposition temperature, respectively. The extracted activation energies of the PureB deposition in each linear region are indicated in Fig. 2. For the deposition in H<sub>2</sub> and T  $\leq$  400 °C, the activation energy is found to be 28 kcal/mol. In this region, the forward direction of reactions (R7) and (R8) are not dominant. Therefore, less hydrogen is released from the surface and most of the surface sites are terminated by hydrogen. This has the consethat the deposited PureB-layer is initially quence discontinuous and for longer deposition times, a lumpy layer is created. This is supported by the ellipsometry measurements listed in Table II for PureB layers deposited on a smooth PureB-layer pre-deposited at 700 °C. This first layer has a roughness <0.2 nm, while the low-temperature layers have higher roughness. For the temperature range from 400 to 700 °C, the activation energy is found to be 6.5 kcal/mol. In this region, the deposition of the PureB layer is mainly controlled by reactions (R3) and (R5). Since reactions (R7) and (R8) are more in the forward direction, the surface hydrogen is swept away by these reactions. Then the surface H coverage is very low, and accordingly, the deposited PureB layer in this temperature region is very smooth and uniform as confirmed by the ellipsometry measurements in Table II. At higher temperatures above 700 °C, the deposition rate decreases with increasing temperature. This is largely due to a rise in desorption of boron atoms from the surface (reverse direction of reactions (R3)–(R6)). Moreover, more boron can be lost from the surface by diffusion into the silicon substrate as given by reaction (R14). In Fig. 3, measured sheet resistance values are plotted as a function of deposition temperature. The values decrease with temperature with a very significant drop starting around 750 °C where the boron diffusion constant in Si increases significantly. Sarubbi et al.<sup>1</sup> have shown that the PureB layer has very high resistivity and the sheet resistance at these deposition temperatures is determined by the doping of the Si that is limited by the deposition time and the boron solid solubility in Si.

In the case of deposition in  $N_2$ , there is no hydrogen for suppressing the forward direction of the reactions (R7) and

TABLE II. PureB-layer roughness extracted from ellipsometry measurements, for a layer deposited in H<sub>2</sub> onto a smooth PureB-layer pre-deposited at 700 °C. This first layer has a roughness < 0.2 nm.

	Temperature range (°C)		
	T < 400	$400{\leq}T{\leq}700$	T > 700
Measured roughness (nm)	0.6–0.9	0.2–0.5	0.4–0.7



FIG. 3. Measured sheet resistance at different deposition temperatures for the diborane partial pressure,  $P_{high} = 3.39$  mTorr.

(R8); therefore, the activation energy is low with a value found to be 2.1 kcal/mol. This value is determined by the actual  $BH_3$  reactions with Si and B surface sites.

All in all, it can be concluded that the boron deposition occurs through four main mechanisms: (a) direct B deposition by decomposition of BH<sub>3</sub> at free Si/B sites (R3)-(R6), (b) the intermediate reaction of atomic hydrogen with the Hterminated Si/B surface sites to release H<sub>2</sub> and create free Si/ B sites ((R7) and (R8)), (c) post-deposition reactions by cross-linked processes accompanied with H<sub>2</sub> split-off (R9)-(R11), and (d) B desorption from the surface (reverse of (R3)-(R6)). The process (c) is associated with decomposition of bulk H-Si and H-B bonds to give H<sub>2</sub> evolution as has been observed in annealing experiments such as the one reported by McMillan and Peterson<sup>31</sup> for a-Si:H thin film treatments. During the deposition, all four mechanisms (a), (b), (c), and (d) occur simultaneously. At the lower temperatures, (b) and (c) proceed slower than (a), and a hydrogenated layer may form near the surface. At the more moderate temperatures, there is a better balance between the three steps (a), (b), and (c). Process (d) becomes dominant at high temperatures and the deposition rate decreases significantly.

The comparison between  $H_2$  and  $N_2$  carrier gases given in Fig. 2 shows that the presence of  $H_2$  is inhibiting the deposition, i.e., the reactions (R3)–(R10) are suppressed in the forward direction. Therefore, it can be concluded that for the inert carrier gas  $N_2$ , the deposition rate is determined by the rate of desorption of hydrogen being supplied by the precursor gas  $B_2H_6$ .

In conclusion, it has been shown that, based on the presented results, the CVD behavior of boron on silicon from diborane to form PureB layers can be understood in terms of the detailed reaction mechanisms involving BH<sub>3</sub> and H reactions with either Si or B surfaces. Desorption of H from surface bonds is essential for obtaining smooth layers with high deposition rates. Therefore, at 400 °C, the highest rate of ~0.3 nm/min is found with a N<sub>2</sub> rather than H<sub>2</sub> carrier gas. The latter prevents deposition at temperatures below 400 °C if the B<sub>2</sub>H<sub>6</sub> partial pressure is too low. Activation energies have been determined in three distinguishable regions that each can be related to the dominance of a different chemical reaction mechanism: for H<sub>2</sub> as carrier gas, 28 kcal/mol is found below 400 °C and 6.5 kcal/mol from 400 °C to 700 °C; for N<sub>2</sub> as carrier gas, the activation energy is found to be 2.1 kcal/mol for all deposition temperatures below 700 °C.

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