# A Simple Model describing the kinetic of CVD Deposition of Pure-Boron Layers from Diborane

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In this paper, an analytical model is established to describe the deposition kinetics and the deposition chamber characteristics that determine the deposition rates of PureB-layers grown by chemical-vapor deposition (CVD) from diborane ( $B_2H_6$ ) as gas source on a non-rotating 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. This model is based on a wide range of input parameters, such as initial diborane partial pressure, total gas flow, axial position on the wafer, deposition temperature, activation energy of PureB deposition from diborane, surface H-coverage and reactor dimensions. The model's predictive capabilities have been verified by experiments performed at 700 °C in these two different ASM CVD reactors.

#### Introduction

The chemical-vapor deposition of pure boron has in the last years been very successfully applied for fabricating extremely shallow, less than 10-*nm* deep, silicon  $p^+n$  junction diodes for a number of leading-edge device applications (1). This so-called PureB technology has provided particularly impressive performance of photodiode detectors for low penetration-depth beams for which 2-nm-thick PureB-layers are reliably implemented as the front-entrance window (2-5). Ideal low-leakage diode characteristics are achieved for deposition temperatures from 400°C - 700°C, which together with the fact that the deposition is conformal and highly selective to Si, also makes PureB technology an attractive candidate for creating junctions on silicon nanowires and advanced CMOS transistors including source/drain in p-type FinFETs (6, 7). In the latter applications, sub-3-nm thick layers are required to avoid excess series resistance through the high-resistivity boron layer. Moreover, for the photodiode application any thickness variations even in the angstrom range can have a large impact on the responsivity to beams that only penetrate a few nm into the Si such as VUV light and less-than 1 keV electrons. Therefore, a very good control of the layer thickness is crucial.

The PureB deposition is susceptible to loading effects and strongly depends to the deposition and reactor conditions (8). In order to achieve better control of the deposition and an understanding of the associated kinetics, the deposition mechanism and growth characteristics should be described.

In recent years, various theories have been proposed to describe the transport phenomena in CVD reactors (9-11). Most of these have modeled the epitaxial growth of Si and SiGe layers, and they can be divided into two main groups. The first covers models that were developed on the basis of the boundary-layer theory and only consider physical diffusion effects (e.g. 9). The second encompasses models that consider the surface reactions (e.g. 10, 11). Since in CVD reactors the boundary layer is stationary or at most moving slowly, the input value of partial pressure of the reactants cannot be upheld throughout the chamber. Moreover, the design of the chamber (the height and width of chamber, the size of the susceptor, etc.) can also have an influence on the deposition and the final growth rate of the layer. For modeling that is detailed enough to be predictive it is necessary to consider both physical phenomena and reaction processes in relationship to the specific reactor design.

In this paper, a kinetic model is purposed and shown to be potent enough to predict the rate of pure-boron deposition from diborane  $(B_2H_6)$  on a non-rotating silicon wafer. The model takes into consideration the gas-phase diffusion mechanism of the diborane species through the stationary boundary layer over the wafer, the gas phase processes and the related surface reactions.

#### Analytical kinetic model

In Fig. 1 a schematic illustration is shown of the chemical and physical CVD chamber geometry that we have used in our model. In the modeling reactor the height, h, is constant and equal to 22 mm and the width, b, is much larger than h. The aspect ratio,  $h/b \approx 0.085$ , is therefore so small that we can consider this reactor to be a two-dimensional system with sufficient accuracy.



Figure 1. Schematic illustration of the CVD reactor geometry used for modelling purposes.

This 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. The concentration profile of the reactant species in the horizontal chamber of the ASM Epsilon One CVD reactor is developed for diffusion controlled growth rates in a laminar flow system. In the following treatments, the gas flow is considered to be laminar and dominated by forced convection. By solving the equation for mass conservation for the isothermal system as outlined in appendix A, the equation 1 as the average concentration profile of the reactants over the susceptor with linear velocity profile is obtained

$$\overline{C}(x) = 0.692C_0 \exp\left(\frac{-2.52D}{h^2 u_0}x\right)$$
<sup>[1]</sup>

In this equation, D is the gas phase diffusivity of diborane molecules in the hydrogen.  $C_0$ ,  $u_0$  are the initial diborane concentration and velocity of gases and h and x are the height of chamber and axial position over the wafer, respectively.

From Meng Tao approach (10) for the PureB case, the activated flux of a precursor, i.e., the number of boron species that decomposes upon collision with the substrate is:

$$f_R^S = \frac{P_R^S}{\left(2\pi n_B k_b T\right)^{\frac{1}{2}}} \left(\frac{E_A}{k_b T} + 1\right) \exp\left(-\frac{E_A}{k_b T}\right)$$
[2]

where  $P_R^S$  is the partial pressure of the reactant at the surface of the substrate, and  $E_A$  is the activation energy of the heterogeneous reaction, and assuming an ideal gas with CV independent on temperature and pressure for which  $P = Nk_bT$ . In the case of PureB deposition from diborane, B<sub>2</sub>H<sub>6</sub>, possible reactions to consider are listed in Table I.

**TABLE I.** Heterogeneous reaction possibilities involved in PureB-layer CVD deposition with  $B_2H_6$  as a precursor.

Deastion	Notation	DIL reaction with	Departies
Reaction	Notation	$\mathbf{D}_{2}\mathbf{\Pi}_{6}$ reaction with	Reaction
no.			
[R1]	$f_{B_2H_6-on-Si}$	H-free Si surface sites	$B_2H_6 + 2(\circ Si) \Longrightarrow 2(H_2B - Si) + 2H$
[R2]	$f_{B_2H_6-on-HSi}$	H-terminated Si surface sites	$B_2H_6 + 2(H - Si) \Longrightarrow 2(H_2B - Si) + 2H_2$
[R3]	$f_{B_2H_6-on-B}$	H-free PureB surface sites	$B_2H_6 + 2(\circ B) \Longrightarrow 2(H_2B - B) + 2H$
[R4]	$f_{B_2H_6-on-HB}$	H-terminated PureB surface sites	$B_2H_6 + 2(H-B) \Longrightarrow 2(H_2B - B) + 2H_2$

The activation energies for reactions on H-terminated Si/PureB surface sites are larger than H-free sites (12). Thus these fluxes can be neglected as compared to those on H-free Si/PureB surface sites. As mentioned in ref. (7), at the early stages of deposition, such as sub-min deposition times, boron atoms are deposited and interact to cover the silicon surface with an atomic-layer plane and the boron coverage can also grow to exceed one monolayer (1 ML). Thus the PureB deposition can be divided into the two stages. In the first stage a monolayer coverage of pure-boron atoms on the Si surface is being built up and in the second stage the pure-boron atoms are deposited on a surface fully covered with boron atoms. Here only second stage is modeled. Under these assumptions, the total surface B flux can be expressed as

$$f_B^S = f_{BH_3-on-Si}^S + f_{BH_3-on-HSi}^S + f_{BH_3-on-B}^S + f_{BH_3-on-HB}^S$$

$$\approx f_{BH_3-on-Si}^S + f_{BH_3-on-B}^S$$

$$\approx f_{BH_3-on-B}^S$$

$$[3]$$

Then based on equation 2, we can write down the equation for the primary surface B flux as

$$f_{B}^{S} \approx \eta \gamma \left(1 - \theta_{H(B)}\right) \frac{P_{BH_{3}}^{S}}{\left(2\pi n_{BH_{3}} k_{b} T\right)^{\frac{1}{2}}} \left(\frac{E_{BH_{3}-on-B}}{k_{b} T} + 1\right) \exp\left(-\frac{E_{BH_{3}-on-B}}{k_{b} T}\right)$$
[4]

In this equation,  $\theta_{H(B)}$ ,  $P_{BH_3}^S$  and  $m_{BH_3}$  are the ratio of the H-terminated PureB surface sites to all the PureB surface sites, the BH<sub>3</sub> partial pressure at the substrate surface, and molecular mass of BH<sub>3</sub>, respectively. The  $E_{BH_3-on-B}$  is the activation energy of the PureB CVD deposition (12) unique to the particular reaction [R3]. The  $\gamma$  is the ratio of PureB surface sites to all surface sites and is calculated as [B]/N<sub>0</sub>, where [B] is the B concentration and N<sub>0</sub> the atomic density of the PureB-layer, which is  $5.0 \times 10^{22}$  atoms/cm<sup>3</sup> at Si surfaces and  $1.3 \times 10^{23}$  atoms/cm<sup>3</sup> at PureB surfaces (13). Also  $\eta$  *is* a unit less constant.

With equations 1 and 4 and using the ideal gas law in a very thin layer over the susceptor, the deposition rate, *Dep.Rate*, of the PureB-layer deposited in a CVD system by using  $B_2H_6$  can be calculated as

$$Dep.Rate(x) \approx 0.264\eta\gamma \frac{\left(1 - \theta_{H(B)}\right)}{N_0} \frac{P_{BH_3}}{\left(m_{BH_3}k_bT\right)^{\frac{1}{2}}} \left(\frac{E_{BH_3-on-B}}{k_bT} + 1\right)$$

$$\times \exp\left(-\frac{E_{BH_3-on-B}}{k_bT}\right) \exp\left(-\frac{2.52D}{h^2u_0}x\right)$$

$$(5)$$

In this equation, the  $P_{BH_3}$  is the input partial pressure of the  $BH_3$ .

## **Experiments and Results**

Experiments were carried out in two systems, the ASM Epsilon One and 2000, that have a quartz reactor with a rectangular cross-section. These reactors have a large SiC susceptor which is heated up to the deposition temperature by a crossed array of lamps above and below of the deposition chamber. For deposition of the PureB-layer, diborane was used as a gas source with different input partial pressures from 1.7 to 3.39 *mtorr*. Pure H<sub>2</sub> was used as a carrier gas with a water and oxygen content below the *ppm* level with variable flow rates between 5 to 20 slm (standard liter per minute). All depositions were performed at 700°C and atmospheric pressure (ATM) over 100 mm non-rotating bare Si (100) wafers with a thickness of 500-550  $\mu$ m.

In Fig. 2 several experimental results are compared to model predictions. It should be noted that parameter fitting was performed for the ASM Epsilon One. The PureB deposition rates are extracted as a function of (a) the axial position, x, for different gas flow and diborane partial pressure conditions, (b) gas flow over the susceptor, and (c) input diborane partial pressure including curves for two different axial positions. By only adjusting the reactor/process parameters, this model was also successfully transferred from the ASM Epsilon One to the Epsilon 2000 reactor which has totally different reactor conditions. The experimental results and model predictions for the Epsilon 2000 are also shown in Fig. 2a. In fact, this model has the capability to predict the deposition rate on any 2-D uniform or non-uniformly patterned wafer such as those used for advanced device fabrication. A very small, less than 5%, deviation between experimental results



and model prediction is plausibly related to the lateral diffusion of the diborane atoms and it becomes more evident at lower gas flows and diborane partial pressures.

Figure 2. Model and experimental results for the PureB deposition rate as a function of (a) an axial position, x, (b) main gas flow over the susceptor, and (c) diborane partial pressure. The applied diborane partial pressures were 3.39, 2.55 and 1.7 *mtorr* given by P<sub>1</sub>, P<sub>2</sub> and P<sub>3</sub>, respectively. And the applied gas flows were 20, 15 and 10 *slm* given by F<sub>1</sub>, F<sub>2</sub> and F<sub>3</sub>, respectively. All experiments were performed at atmospheric pressure.

It can be seen that the data calculated on the basis of this model fits well with the experimental results and it has been very useful in the development of uniform PureB-layers with little pattern dependence as well as for transferring recipes from one reactor to the other.

#### Conclusions

In this paper, an analytical model was developed to describe the deposition kinetics and the deposition chamber characteristics that determine the deposition rate of PureB layers over the wafer. This model is based on a wide range of input parameters, such as initial diborane partial pressure, total gas flow, axial position on the wafer, deposition temperature, activation energy of diborane deposition, surface H-coverage and reactor dimensions. By only adjusting these reactor-process parameters, this model was also successfully transferred from the ASM Epsilon One to the Epsilon 2000 reactor which has totally different reactor conditions. The deposition of 2-nm-thick PureB-layers with only a few angstrom thickness variations is now performed standardly for a variety of process wafer conditions (8).

## Appendix A

In this Appendix, the outline of the derivation of equation 1 is presented. Details can be found in ref. (14).

First we consider a system with a constant temperature in which the active component rapidly decomposes at the susceptor, y = 0, for all axial flow positions  $x \ge 0$  (Fig. 1). Therefore, the concentration at y = 0 is zero across the whole decomposition zone. Transport of material towards the susceptor in the y-direction goes entirely via gasphase diffusion (laminar flow through the stationary boundary layer over the susceptor). The equation for mass conservation for this case is:

$$u(y)\frac{\partial C(x,y)}{\partial x} = D\frac{\partial^2 C(x,y)}{\partial y^2}$$
[6]

where C(x,y) and D are the concentration profiles and the gas-phase diffusion coefficient of the active component in the carrier gas respectively u(y) is an expression for the parabolic velocity profile in the reactor chamber and given by:

$$u(y) = 4u_0 \left(\frac{y}{h} - \frac{y^2}{h^2}\right)$$
<sup>[7]</sup>

Equation 6 is difficult to solve for a parabolic velocity profile. Therefore, the problem is first to be solved for a constant flow velocity thereafter the influence of a parabolic flow profile on the obtained results is evaluated. For the case of a constant flow velocity  $(u_0)$  the problem can be solved analytically to reach a summation equation (see ref. 14). After simplification, equation 8 can be calculated for the concentration profile:

$$C(x, y) = \frac{4C_0}{\pi} \sin\left(\frac{\pi y}{2h}\right) \exp\left(\frac{-\pi^2 D}{4h^2 u_0}x\right)$$
<sup>[8]</sup>

In this equation, the gas phase depletion in the flow direction is represented by the exponential term. The axial distance  $x_0$  at which the concentration at y = h reaches the critical concentration of  $0.99C_0$  after correction for the linear velocity profile can be extracted as (14):

$$x_0 = \frac{h^2 u_0}{16D}$$
[9]

Equation 8 shows that in the development region  $x \le x_0$  the largest drop in concentration occurs in a relatively thin layer above the susceptor. E.g. at y = h/4 the concentration drop is down to the approximately 42%. Therefore, for calculation of the mass flux at y = 0, this part of the reactor represents the region of main interest. The main concentration drop occurs between y = 0 and y = h/4. In order to solve equation 6 in a more realistic way than the plug velocity approach given above, the parabolic velocity profile can be substituted by a linear velocity distribution as

$$u(y) = 3.4u_0 \left(\frac{y}{h}\right) \tag{10}$$

This is on the average correct to within ~ 10% in the relevant range  $0 \le y \le h/4$  as illustrated by Fig. 3.



Figure 3. Parabolic flow profile of equation 7 for  $x_0 = \frac{h^2 u_0}{16D}$  (solid line) and linear velocity approximation of equation 10 (dashed line) as a function of *y* for  $0 \le y \le h/4$ .

Following ref. (15) for the solution of the diffusion problem in a semi-infinite system with a capturing boundary at y = 0, and using Fick's law gives

$$F_m(x) = 0.81 D C_0 \left(\frac{Dhx}{u_0}\right)^{-\frac{1}{3}}$$
[11]

Because the active component is only consumed at y = 0 (over the susceptor), the average concentration at  $x = x_0$ ,  $\overline{C}(x_0)$ , can now be calculated on the basis of the total amount of material that has disappeared as follows:

$$\int_{0}^{x_{0}} F_{m}(x) dx = h u_{0} \Big[ C_{0} - \overline{C}(x) \Big]$$
[12]

Solving this equation and using equations 11 and 9 gives the concentration profiles at y = 0 presented in equations 1

$$\overline{C}(x) = 0.692C_0 \exp\left(\frac{-2.52D}{h^2 u_0} x\right)$$
[1]

This is the average concentration profile of the reactants over the susceptor with linear velocity profile. This will be used for developing the final deposition rate model for PureB layer deposition.

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