Lateral gas phase diffusion length of boron atoms over Si/B surfaces during CVD of pure boron layers

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The lateral gas phase diffusion length of boron atoms, \( L_B \), along silicon and boron surfaces during chemical vapor deposition (CVD) using diborane (\( \text{B}_2\text{H}_6 \)) is reported. The value of \( L_B \) is critical for reliable and uniform boron layer coverage. The presented information was obtained experimentally and confirmed analytically in the boron deposition temperature range from 700 °C down to 400 °C. For this temperature range the local loading effect of the boron deposition is investigated on the micro scale. A \( L_B = 2.2 \) mm was determined for boron deposition at 700 °C, while a \( L_B \) of less than 1 mm was observed at temperatures lower than 500 °C.

I. INTRODUCTION

Pure boron (PureB) layers deposited on silicon by the chemical vapor deposition (CVD) technique in the temperature range from 400 °C (low temperature, LT) to 700 °C (high temperature, HT) have in recent years been very successfully applied to create the \( \text{p}^+ \)-region of extremely shallow, less than 10 nm deep, silicon \( \text{p}^+ \text{n} \) junction diodes for a number of cutting edge device applications.1–5 The possibility of LT boron layer deposition makes LT PureB technology highly compatible with thin film amorphous/polysilicon/crystalline-silicon device processing and allows for the full integration of LT PureB photodiodes into electronic interface circuits and other sensors on a single chip. In this way, smart sensor systems and even CMOS UV imagers can be realized. LT technology can be also used for creating an end-of-line capping layer to passivate the surface of fully processed CMOS imagers and increase their spectral sensitivity range from IR down to soft X-ray.

A particularly impressive performance of Si photodiodes with a sensitive area in the millimeter scale has been achieved for low penetration depth beam detection.1,3,6,7 Other applications which may profit from this technology are \( \text{p} \text{n} \) junctions on the micrometer scale, e.g. advanced CMOS transistors including source/drain in \( \text{p} \)-type FinFETs.8,9 For both millimeter- and micrometer-sized applications, a reliable and uniform sub 3-nm-thick boron layer is required to avoid excess series resistance through the highly resistive boron layer.10 Moreover, any thickness variations even in the angstrom range can have a large impact on device performance. Therefore, very close monitoring of the layer thickness is crucial.

In previous works11,12 we have demonstrated that boron deposition is susceptible to loading effects and is pattern-dependent due to the selectivity of the deposition between the Si and \( \text{SiO}_2 \) surfaces where the lateral gas phase diffusion length of boron atoms over \( \text{SiO}_2 \) and/or Si/B surfaces plays an important role. The lateral gas phase diffusion length of boron atoms was determined for \( \text{SiO}_2 \) surfaces to be about 1.5 cm.11 However, there is no information available for the lateral gas phase diffusion length of boron atoms over Si/B surfaces. Yet this parameter is needed for developing our previously proposed analytical kinetic model which functions as a comprehensive model to predict the boron deposition rate and the profile on any 2D uniformly or non-uniformly patterned wafers, such as those used for advanced device fabrication.13

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To bridge this gap, in this paper, the local loading effect of the boron deposition is investigated on the micro scale to understand the uniformity profile of the deposited boron layer inside the oxide opening. The diffusion length of boron atoms $L_B$ along the silicon and boron surfaces was determined experimentally and analytically. $L_B$ presents the average distance that boron atoms can travel along the silicon and boron surfaces before deposition or desorption to the main gas stream occurs. The derived analytical value of $L_B$ corresponds well with the experimental data.

II. EXPERIMENTAL PROCEDURE

The experiments were carried out in the ASM Epsilon 2000 Si/SiGe epitaxial reactor. The PureB deposition is performed by using diborane (B2H6) with a concentration of 0.2% as a gas source and hydrogen as both carrier gas and dilutant. The deposition temperature varies from 400 °C, referred to here as “low-temperature (LT)”, to 700 °C, the “high-temperature (HT)” to investigate the effect of temperature on the diffusion length of boron atoms ($L_B$) along the silicon and boron surfaces.

The test structure used for this purpose is shown in Fig. 1. This test structure is a combination of the vertical resistance measurement structure as described by V. Mohammadi et al. and a modified version of the test structure employed by V. Mohammadi et al. The modification consists of substituting the reference die where the boron is deposited with a resistance measurement structure with a width of $W_{Si} = 20$ mm. The reference die is then surrounded by rings of oxide with a width of $W_{ox}$. As shown in Fig. 1, this oxide ring is surrounded by an open Si ring that has the function of isolating the central reference die from any loading effects other than those supplied by this ring.

The local oxide ratio ($LOR = W_{ox}/W_{si}$) is realized by changing the width of the oxide ring, $W_{ox}$. The resistance measurements are done using an array of $190 \times 190$ contacts over the boron layer deposited inside the die. Thereafter the measured resistance is converted into boron layer thickness by using the expressions given in Ref. 14, and are used to monitor the layer profile. A linear relation between the measured resistance and the boron thickness, regardless of the contact size, provides a handy tool for thickness measurements, while the fine resolution of the measurements makes it very useful for 2D monitoring of the boron layer uniformity inside the opening in relation to the local oxide ratio. This way the diffusion length of boron atoms over Si/B surfaces can be found from thickness gradient of the boron layer.

III. ANALYTICAL DERIVATION

To determine $L_B$ precisely, an analytical calculation was performed. The analytical result was then compared with the experimental data and the exact value of $L_B$ was determined. Figure 2 shows a schematic illustration of a boron concentration profile over a semi-infinite Si window and adjusted oxide area, when there is no lateral boron reaching the other side of the Si window. In this figure, $C_{last}$ represents the concentration of boron atoms accumulated over the oxide area at the edge of Si opening ($x' = 0$); and $C_V$ is the concentration of boron atoms supplied by the vertical component.
Eq. (1), which illustrates the boron atoms coming directly from the main gas flow during the layer deposition.\textsuperscript{13}

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

The lateral concentration of the boron atoms, \( C_L(x') \), can be calculated by solving the time-independent diffusion equation of Eq. (2) in the steady state:

\[ L_B^2 \frac{\partial^2 C_L}{\partial x'^2} - C_L = 0 \] (2)

where \( L_B \) is the diffusion length of boron atoms, and \( x' = 0 \) is located at the edge between the Si opening and the oxide area, as shown in Fig. 2.

The general solution of Eq. (2) is:

\[ C_L(x') = k_1 \exp \left( - \frac{x'}{L_B} \right) + k_2 \exp \left( \frac{x'}{L_B} \right) \] (3)

where \( k_1 \) and \( k_2 \) are constants to be determined based on the boundary conditions of Eq. (4) as schematically illustrated in Fig. 2. In this semi-infinite Si window the boundary conditions would be:

\[
\begin{cases}
C_L(x' = 0) = \bar{C}_{L,ox} \\
C_L(x' = \infty) = 0
\end{cases}
\] (4)

By applying these boundary conditions in Eq. (3) the lateral concentration of the boron atoms can be expressed by:

\[ C_L(x') = \bar{C}_{L,ox} \exp \left( - \frac{x'}{L_B} \right) \] (5)

As can be seen in Fig. 2, \( \bar{C}_{L,ox} \) is the boron concentration over the oxide area at \( x' = 0 \) which is due to accumulation of boron atoms supplied by the main gas flow over this oxide area with a width of \( W_{ox} \). Therefore it can be expressed as:

\[ \bar{C}_{L,ox} = \int_{W_{ox}} \bar{C}_V(x_{ox}) \, dx_{ox} \] (6)
Solving Eq. (6) using Eq. (1) as a vertical component of boron atom concentration and the only source of boron atoms over the oxide covered surfaces gives:

\[ \bar{C}_{Lo,x} = \frac{0.275\zeta h^2u_0C_0}{D} \exp\left(-\frac{12.6D}{h^2u_0}\right) \times \sinh\left(\frac{2.52D}{h^2u_0}W_{ox}\right) \]  

(7)

The \( \zeta \) is a unit less constant.

By following the derivation procedure presented by Ref. 13 and using Eqs. (5) and (7), the boron deposition rate, DR, in this particular case, can be expressed as:

\[ DR_B^L(x) = \zeta \beta_1 \beta_2 A_2 P_{BH3} \sinh\left(\frac{2.52D}{h^2u_0}W_{ox}\right) \times \exp\left(-\frac{x'}{L_B}\right) \]  

(8)

where:

\[ \beta_1 = \eta \gamma \frac{1}{N_0} \left(1 - \theta_{BH}\right) \left(m_{BH3}kT\right)^{1/2} \]

\[ \beta_2 = \left(\frac{E_{BH3-on-B}}{kT} + 1\right) \exp\left(-\frac{E_{BH3-on-B}}{kT}\right) \]

\[ A_2 = 0.105 \times \frac{h^2u_0}{D} \times \exp\left(-\frac{12.6D}{h^2u_0}\right) \]

Therefore \( L_B \) can be determined by plotting DR on a logarithmic scale versus the position inside the die as will be discussed later.

IV. RESULTS AND DISCUSSION

The 2D contour plots of the boron layer uniformity extracted experimentally by using test structure of Fig. 1 are shown in Fig. 3 for different local oxide ratio (LOR) values: 0, 0.03, 0.06, 0.1, 0.3, 0.4, 0.5, 0.75, 1, and > 2. The boron layer was deposited by a standard 12-min deposition at 700 °C performed inside an Epsilon 2000 CVD reactor. In this figure the impact of the local loading effect on the final deposited layer thickness is clearly visible as it becomes stronger for high values of the LORs (LOR > 0.1). As can be seen for LOR values of less than 0.1 there is no significant thickness variation due to this narrow oxide area, while at LOR = 0.1 the overall layer thickness is increased but still no measurable non-uniformity can be seen. However, the local loading effect increases considerably with increasing LOR values greater than 0.1, which causes more layer non-uniformity as can be clearly seen in Fig. 3. From these graphs, the gradually decreasing layer thickness from the oxide side to the middle of the window can be seen. It can be deduced that the boron thickness is almost symmetrical with respect to the center of the die in any symmetrical designs. It is thinner in the middle, thicker at the edges where it is adjacent to the oxide, and thickest at the corners of the window where it is adjacent to the oxide on two sides. Upon closer look at these graphs, from the color gradient at the edge of the openings, it can be found that the diffusion length of boron atoms, \( L_B \), is roughly \( \sim \) 3 mm.

The precisely value of \( L_B \) can be determined by using the analytical equation of (8) as shown in Fig. 4. To remove the effect of the vertical component of the source of the boron atoms inside the Si window opening that comes directly from main gas stream, the experimental data of LOR = 0 is subtracted from the experimental data of LOR = 0.3. For LOR = 0 there is no oxide ring in the test structure of Fig. 1, therefore only the vertical component is monitored. As can be seen in Fig. 4, the dashed line predicted by the model from Eq. (8) follows the experimental data satisfactorily for values of \( x \) lower than 4 mm. In this case the calculated value of \( L_B \) is 2.2 mm. The deviation of
FIG. 3. 2D contour plot of the boron layer uniformity of the test structures in Fig. 1, for different local oxide ratio (LOR) values. The boron was deposited with a standard 12-min deposition at 700 °C inside an Epsilon 2000 CVD reactor.

the experimental data from the model values, seen clearly for values of \( x \) higher than 4 mm, can be explained by the fact that a semi-infinite opening was assumed as the boundary condition of Eq. (4) and Fig. 2. In reality and particularly in the test structure, there is also a loading effect from the oxide area on the other sides of the Si opening which causes the deviation.

The value \( L_B = 2.2 \text{ mm} \) means that the boron atoms can travel laterally along the silicon or boron surfaces for an average of about 2.2 mm before they disappear due to deposition or desorption. Therefore it can be concluded that for \( W_S < L_B \), regardless of the LOR value, the local loading effect does not have any significant influence on the uniformity of the final layer deposited because the boron atoms can easily pass through the opening. Therefore the layer profile of these openings would be uniform with almost no thickness variations between the side and the middle of the opening. This can be seen in Fig. 5, where the 2D contour plot of the normalized boron thickness
FIG. 4. Model and experimental results for the lateral component induced boron deposition rate as a function of the axial position inside the Si opening. The model values are calculated based on Eq. (8). The lateral component is determined by subtracting the experimental data of LOR = 0 from the experimental data of LOR = 0.3.

 deposited inside the segments of the back-scattered electron detector structure designed by the authors of Ref. 3 is presented. In this structure the LOR > 0.1 while $W_{Si} < L_B$ and the concave profile of deposited boron layer is not visible. This figure is derived from low energy electron beam (LEEB) measurements. For $W_{Si} > L_B$, the amount of local loading effect is dependent on the LOR value of the device layout as investigated by Ref. 12 and also seen in Fig. 3.

At lower deposition temperatures ($< 700^\circ$C), the value of $L_B$ drops dramatically due to a smaller amount of available energy to promote the intermediate reactions during the CVD of boron. This can be seen in Fig. 6 where 2D contour plots of the normalized boron layer uniformity are shown for boron layers deposited at 500 $^\circ$C and 400 $^\circ$C over the test structure with a LOR = 0.5.

FIG. 5. 2D contour plot of the normalized boron thickness deposited inside the segments of the back-scattered electron detector structure designed by Ref. 3. The die size is 10 × 10 mm$^2$, $\phi = 4$ mm, $W_{Si} = 0.9$ mm and $W_{ox} = 0.1$ mm.
FIG. 6. 2D contour plots of the normalized boron layer uniformity for boron layers deposited at (a) 500 °C and (b) 400 °C over the test structure with a LOR = 0.5. A more detailed view of the areas surrounded with red dots is shown in Fig. 7.

FIG. 7. Close-up views of the 2D contour plots given in Fig. 6 at the edge of the window near the oxide area.

The higher resolution contour plots of the closed areas with red dots in Fig. 6 are shown in Fig. 7. These contour plots explicitly show the non-uniformity of the profile at the edge of the window near the oxide area, where a value of less than 1 mm can be obtained for \( L_B \).

V. CONCLUSIONS

To summarize, the lateral gas phase diffusion length of boron atoms \( L_B \) along silicon and boron surfaces was determined for boron CVD deposition for the temperature range from 700 °C to 400 °C experimentally and analytically. A \( L_B = 2.2 \) mm was calculated for boron deposition at 700 °C, while it was reduced to less than 1 mm for deposition at lower temperatures (<500 °C). It was shown that for the Si openings with \( W_{Si} < L_B \), regardless of the LOR value, the local loading effect does not result in any significant non-uniformity in the final deposited layer, because the boron atoms can easily pass the opening.

The local loading effect of the boron deposition was investigated in this temperature range on the micro scale to understand the uniformity profile of the deposited boron layer inside the opening. The investigation showed that for LOR values of less than 0.1 there is no significant thickness variation due to the narrow oxide area, while at LOR = 0.1 the overall layer thickness is increased but still no measurable non-uniformity can be seen. However, the local loading effect rises considerably with increasing LOR values of more than 0.1.
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