A Simple Model for the Deposition of Boron in Silicon by Using a BN Diffusion Source

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ABSTRACT

A physical model based on the multiple charge state vacancy statistics is proposed to express the boron diffusivity in silicon during the deposition step using the BN disk as a diffusion source in an inert ambient. The diffusion equation with concentration dependent diffusivity is solved numerically. A universal shape of the normalized profiles is observed. The surface concentration of the deposited layer has been determined experimentally. The calculated sheet resistance as a function of deposited time and temperature is in good agreement with the measured data. With a slight modification, this simple vacancy statistics model can also be applied to other deposition sources.

One of the most important advantages of the boron nitride (BN) source deposition process is its high reproducibility. It is also possible to describe the deposition sheet resistance in mathematical terms. As found by Armigliato et al. (7), although dopant concentration is much higher than the solubility value at deposition temperature, precipitation is hard to occur. It is reasonable to assume that each boron atom in silicon provides a free hole in the diffusion coefficient and sheet resistance calculations. The hole mobility deduced by Antoniadis et al. (8) will be used in the surface concentration and sheet resistance calculations.

Experimental

The diffusion source employed in this work was Carborundum BN-975 boron nitride disks. The silicon materials used were 2 in. diam (111) oriented, one-side polished, high resistivity (>20 k-ohm cm) n-type wafers. The source and silicon wafers are face-to-face with a spacing of approximately 1 mm. The diffusion furnace was Thermco-Ranger Type-3000. The furnace ambient was dry nitrogen at a flow rate of 1 liter/min. The sheet resistance of deposited layers was measured using a Veeco Model FPP-100 four-point probe. In order to obtain information on the dopant profile, the surface concentration was determined from a differential sheet resistance measurement. The thickness of the deposited layer was measured using a Rudolph Auto EL-II ellipsometer. The volumetric ratio of 0.4 for silicon dioxide was measured using a Veeco Model FPP-100 four-point probe. In order to obtain information on the dopant profile, the surface concentration was determined from a differential sheet resistance measurement. The thickness of the deposited layer was measured using a Rudolph Auto EL-II ellipsometer. The volumetric ratio of 0.4 for silicon dioxide was measured using a Veeco Model FPP-100 four-point probe.

Fig. 1. Surface concentration of boron in silicon as a function of temperature.

\[ \frac{10^2}{T} (\text{K}) \]

\[ 7 \times 10^2 \]

\[ 1000 \]

\[ 1200 \]

\[ 1400 \]

\[ 1600 \]

\[ x \text{ This Work} \]

\[ o \text{ Stach and Turley (2)} \]

\[ \times \text{ Armigliato et al. (7)} \]
Diffusion Model

The atomic theory of diffusion for substitutional impurities in silicon is based on the lattice vacancy diffusion mechanism. The effect of equilibrium vacancy concentration variation on the impurity diffusivity was first considered by Hu and Schmidt (9), and an expression of concentration-dependent diffusivity based on single charged state had been derived.

At the present time, it is known that silicon vacancies exist in neutral V and multiple charged states V+, V−, and V=, where the charged vacancy states have definite energy levels in the bandgap (4). The bandgap E tracks the valence band edge Ec:

\[ E_v = E_c + 0.37 \text{ eV} \]  \hspace{1cm} \text{(1)}

while the acceptor levels E+ and E− track the conduction band edge Ec:

\[ E_+ = E_c - 0.57 \text{ eV} \]  \hspace{1cm} \text{(2)}
\[ E_- = E_c - 0.11 \text{ eV} \]  \hspace{1cm} \text{(3)}

as the bandgap narrows with increasing temperature

\[ E_G = E_c - E_v = 1.17 - 4.73 \times 10^{-4} \left( \frac{T^3}{T + 636} \right) \]  \hspace{1cm} \text{(4)}

From the Shockley-Last theory (10), the thermal equilibrium concentrations of vacancies at various charged states C+ (r: +, x, −, −) are related to the Fermi level EF by

\[ C^+ : C^x : C^- : C^= = \exp \frac{E^+ - E_F}{kT} : 1 : \exp \frac{E^- - E_f}{kT} : \exp \frac{2E^+ - E^- - E^=}{kT} \]  \hspace{1cm} \text{(5)}

where the degeneracy effects have been neglected. It has been argued by Shockley and Moll (11) that the equilibrium concentration of neutral vacancies is a function of temperature only while the concentration of charged vacancies is a function of the Fermi level as well. The total vacancy concentration normalized to the neutral vacancy concentration is thus given by

\[ C^T = 1 + \exp \frac{E^+ - E_F}{kT} + \exp \frac{E^- - E_F}{kT} + \exp \frac{2E^+ - E^- - E^=}{kT} \]  \hspace{1cm} \text{(6)}

By the use of Boltzmann approximation

\[ \frac{E^r - E_F}{kT} = \frac{p}{n_i} \]  \hspace{1cm} \text{(7)}

where E1 is the intrinsic Fermi level

\[ E_1 = \frac{E_G}{2} = \frac{E_c + E_v}{2} \]  \hspace{1cm} \text{(8)}

and ni is the intrinsic carrier concentration approximately given (12) by

\[ n_i = 3.87 \times 10^{17} T^{3/2} \exp \left( -\frac{0.605}{kT} \right) \]  \hspace{1cm} \text{(9)}

Equation (6) can be expressed as

\[ C^T = 1 + \beta^+ \left( \frac{p}{n_i} \right) + \beta^- \left( \frac{n_i}{p} \right) + \beta^= \left( \frac{n_i}{p} \right)^2 \]  \hspace{1cm} \text{(10)}

\[ \beta^+ = \exp \frac{E^+ - E_F}{kT} \]  \hspace{1cm} \text{(11)}
\[ \beta^- = \exp \frac{E_1 - E^=}{kT} \]  \hspace{1cm} \text{(12)}

On the assumption that the effective diffusivity is directly proportional to the total vacancy concentration (9), one gets

\[ \frac{Dn}{Dt} = \frac{1 + \beta^+ \left( \frac{p}{n_i} \right) + \beta^- \left( \frac{n_i}{p} \right) + \beta^= \left( \frac{n_i}{p} \right)^2}{1 + \beta^+ + \beta^- + \beta^=} \]  \hspace{1cm} \text{(12)}

where D is the intrinsic diffusivity. The value of D for boron in silicon has recently been determined by Antoniadis et al. (8) as

\[ D = 0.55 \exp \left( -\frac{3.42 \text{ eV}}{kT} \right) \text{ cm}^2/\text{sec} \]  \hspace{1cm} \text{(13)}

under nonoxidized atmosphere.

Numerical Analysis

The classical solution of diffusion equation with constant diffusivity and constant surface concentration is a well-known complementary error function. However, for a high-concentration deposition, the diffusion coefficient is concentration-dependent and no analytic solution is available. Most recently a great deal of attention has been given to the use of computer simulation to determine dopant profiles (13).

For a concentration-dependent diffusivity, the diffusion equation is

\[ \frac{\partial N}{\partial y} = \frac{\partial}{\partial y} \left( D \frac{\partial N}{\partial t} \right) \]  \hspace{1cm} \text{(14)}

This problem should be solved numerically by discretizing the space y and time t coordinates

\[ y = y_j = j \Delta y \quad j = 0, 1, 2, \ldots \]
\[ t = t_1 = i \Delta t \quad i = 0, 1, 2, \ldots \]

and writing the differential Eq. (14) as a set of difference equation (14)

\[ N(y_j,t_i+1) = M[D(y_j+1,t_i)N(y_j+1,t_i) + D(y_j-1,t_i)N(y_j-1,t_i) + [1 - 2MD(y_j,t_i)]N(y_j,t_i)] \]  \hspace{1cm} \text{(15)}

where \( M = \Delta (y/\Delta y)^2 \) is called the mesh ratio and \( D(y_j,t_i) \) is evaluated from Eq. (12) by letting \( p = N(y_j,t_i) > n_i \) and \( \beta = n_i \) for \( N(y_j,t_i) \leq n_i \). The boundary condition for a constant surface concentration deposition is \( N(y_0,t_i) = N_0 \) and the corresponding diffusivity is \( D_0 \). The numerical calculation can be performed on a TI-59 programmable calculator. It would take about 2 hr to generate a profile, if a mesh ratio \( M = 10^4 D_0 \), a space interval \( \Delta y \) of \( \sqrt{4D_0t/10} \), and a time interval \( \Delta t \) of t/100 are chosen.

The calculated profiles of \( N/N_0 \) vs. \( y/\sqrt{4D_0t} \) for several deposition temperatures are shown in Fig. 2. These normalized curves show a universal shape in the high concentration region \( N > n_i \) and a complementary error function tail in the low concentration region \( N < n_i \). It is interesting to note that the universal curve can be expressed as

\[ N = 1 - 0.631 \left( \frac{y}{\sqrt{4D_0t}} \right) - 0.214 \left( \frac{y}{\sqrt{4D_0t}} \right)^2 \]  \hspace{1cm} \text{(16)}

which is in good agreement with the approximate solution for arsenic diffusion in terms of Chebyshev polynomials (15). As a matter of fact, Fair's normalized boron profile [Fig. 3 of Ref. (3)] can also be approximated by Eq. (16) if the space coordinate is normalized to the surface diffusion length \( \sqrt{4D_0t} \).

Results and Discussion

The experimental result of sheet resistance as a function of deposition time at various temperatures are
shown in Fig. 3 along with data reported by Rupprecht and Stach (16). Assuming that boron atoms in the diffused layer are fully ionized, the deposited sheet resistance $R_s$ can be calculated from

$$R_s = \int q\mu_p N dy$$ \hspace{1cm} \text{(17)}$$

where $\mu_p$ is the concentration-dependent hole mobility given (8) by

$$\mu_p = 49.7 + \frac{418}{1 + (N/1.6 \times 10^{17})^{0.7}}$$ \hspace{1cm} \text{(18)}$$

As shown in Fig. 3, the numerically calculated results of sheet resistance are in good agreement with measured values.

Alternatively, Eq. (17) can be expressed as

$$R_s^{-1} = q\mu_p Q$$ \hspace{1cm} \text{(19)}$$

where $\mu_p$ is the average hole mobility and $Q$ is the deposited quantity of boron atoms in silicon per unit area. From numerical calculations it has been found that $\mu_p \approx 54 \text{ cm}^2/\text{Vsec}$ for $N_0 = 2 \times 10^{19} \text{ cm}^{-3}$ and $Q \approx 0.628 N_0 \sqrt{D_0 t}$ for all deposited temperatures used in this work. Therefore, the sheet resistance expression (19) becomes

$$R_s = 9.2 \times 10^{16}/N_0 \sqrt{D_0 t} \Omega/\text{sq}$$ \hspace{1cm} \text{(20)}$$

where $N_0$ and $D_0$ are temperature dependent.

If the junction depth was defined as the distance from the surface at which $N/N_0$ had fallen to $10^{-5}$ in Fig. 2, then

$$y_j = 2.4 \times N_0^{1/4 D_0 t}$$ \hspace{1cm} \text{(21)}$$

This is in approximate agreement with Fair's approximation [Eq. (12) of Ref. (3)].

It is suggested from Eq. (20) and (21) that the surface diffusivity $D_0$ can be determined experimentally by profile fitting or sheet resistance and surface concentration measurements. Some experimentally determined values of $D_0/D_1$ and theoretically calculated curves of $D/D_1$ vs. $N/N_1$ are shown in Fig. 4. The multiple charge state vacancy model proposed in this work gives a result for the low temperature deposition using BN disks as diffusion source in a dry nitrogen ambient. For comparison, the $D_0/D_1$ values for BBr$_3$ sources (7) as deduced from profile fitting are also shown in Fig. 4. Enhanced diffusion is observed. This phenomenon may be explained as follows.

The BBr$_3$ liquid source deposition is generally carried out in an oxidized ambient. This may result in some negative ions in the oxide layer. This surface charge causes the energy band of silicon to bend upward at the surface and the hole concentration $p$ is then enhanced by a Boltzmann factor

$$\frac{p}{N} = e^\Delta$$ \hspace{1cm} \text{(22)}$$

\begin{table}
<table>
<thead>
<tr>
<th>Curve</th>
<th>$T(\degree \text{C})$</th>
<th>$N_0$(cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1000</td>
<td>2.3x10$^{19}$</td>
</tr>
<tr>
<td>2</td>
<td>950</td>
<td>2.1x10$^{19}$</td>
</tr>
<tr>
<td>3</td>
<td>900</td>
<td>1.8x10$^{19}$</td>
</tr>
<tr>
<td>4</td>
<td>850</td>
<td>1.6x10$^{19}$</td>
</tr>
</tbody>
</table>
\end{table}
where $\Delta$ is the amount of energy band bending upward normalized to the thermal energy $kT$ and $N$ is the boron concentration. Taking this into account, the effective diffusivity, Eq. [12], is modified to

$$D \frac{D(\Delta)}{D(0)} = \frac{1 + \beta^+ e^\Delta \left( \frac{N}{N_i} \right) + \beta^+ e^{-\Delta} \left( \frac{N}{N_i} \right)^{-1} + \beta^- e^{-2\Delta} \left( \frac{N}{N_i} \right)^{-2}}{1 + \beta^+ + \beta^- + \beta^\Delta}$$

[23]

where $D(0)$ is the intrinsic diffusivity without energy band bending given by Eq. [13]. In Fig. 4, a band bending of 1 $kT$ shows a good fit for the surface diffusivity of the BBr$_8$ source deposition.

In addition to the neutral vacancy concentration, the intrinsic diffusivity at the surface also depends on the band condition

$$\frac{D(\Delta)}{D(0)} = \frac{1 + \beta^+ e^\Delta + \beta^- e^{-\Delta} + \beta^\Delta e^{-2\Delta}}{1 + \beta^+ + \beta^- + \beta^\Delta}$$

[24]

The effect of band bending on the intrinsic diffusivity is shown in Fig. 5. Due to negatively charged vacancies, the intrinsic diffusivity decreases slightly with a small upward band bending. The values used in this work and the data reported by Fair (6) are also shown in Fig. 5. It is interesting to note that the increase of the enhancement of intrinsic diffusivity in oxidizing ambient with decreasing temperature (8) can be explained by the band bending effect. It is well known (17) that the positive oxide charge near the silicon dioxide-silicon interface increases with decreasing temperature. This positive surface charge will cause a downward band bending and the magnitude of band bending will increase with decreasing temperature. Therefore, Eq. [24] gives a good explanation for the diffusivity enhancement.

**Conclusion**

A simple diffusion model based on the vacancy statistics gives a satisfactory prediction of the behavior of BN source deposition. Although the charged state of lattice vacancies might have a different contribution to the diffusion coefficient, the different behaviors for different diffusion conditions can be explained by a band-bending effect.

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