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## 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 (1). High surface concentrations are generated by the BN diffusion system and anomalous effects have been observed under different diffusion conditions (2). To explain concentration-dependent diffusion in an inert atmosphere, Fair (3) proposed a donor-type mono-vacancy diffusion model and showed that the boron profiles fit a normalized universal curve which is a polynomial approximation to the solution of the diffusion equation with linear concentration-dependent diffusivity.

Recently, it was reported that vacancies in silicon can exist in  $V^+$ ,  $V^-$ , and  $V^=$  charge states, each having a definite energy level in the forbidden bandgap (4). Based on the multiple charge state vacancy statistics, Ho and Plummer (5) have successfully explained the commonly observed enhanced oxidation rates of heavily doped silicon. The purpose of this paper is to illustrate that the same statistics can also be applied to the behavior of high concentration boron deposition in a dry nitrogen ambient.

Although Fair (6) has examined the contribution of each charge state to the total diffusivity, it will be a good approximation that the diffusion coefficient of boron in silicon under an inert atmosphere is directly proportional to the total vacancy concentration. Furthermore, the enhanced diffusions in oxidized ambients can be explained by a surface space charge effect. The electric field factor generally encountered in the diffusivity expression will be omitted, since its variation is very small (from 1.45 to 2) and the localized Fermi level involved in the vacancy statistics might include the localized electric field effect.

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.

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Key words: diffusion model, boron deposition, BN source, vacancy statistics.

### 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 ( $>20 \Omega\text{-cm}$ ) n-type wafers. The source and silicon wafers are edge-stacked in the deposition carrier face to face with a spacing of approximately 1 mm. The diffusion furnace used 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 anodic oxides was measured using a Rudolph Auto EL-II ellipsometer. The volumetric ratio of 0.4 for silicon converted to silicon dioxide and the concentration-dependent hole mobility value of Antoniadis *et al.* (8) were used in the concentration calculation. The measured results of surface concentrations as a function of temperature is shown in Fig. 1 along with other reported data for both BN solid source (2) and BB-liquid source (7).

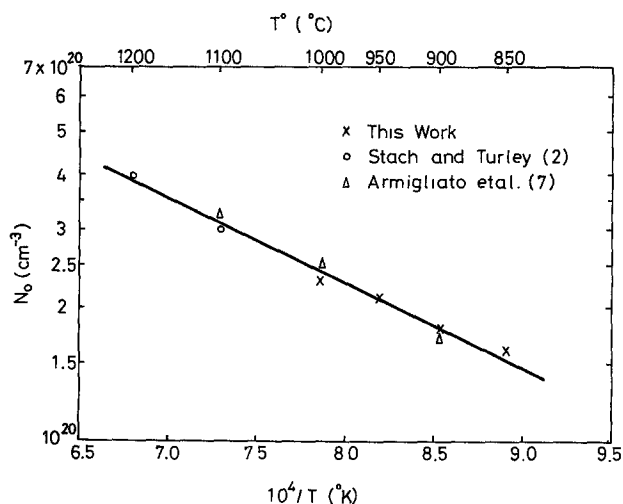


Fig. 1. Surface concentration of boron in silicon as a function of temperature.

### 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  $V^0$  and multiple charged states  $V^+$ ,  $V^-$ , and  $V^{=}$ . The charged vacancy states have definite energy levels in the bandgap (4). The donor level  $E$  tracks the valence bandedge  $E_v$

$$E^+ = E_v + 0.37 \text{ eV} \quad [1]$$

while the acceptor levels  $E^-$  and  $E^{=}$  track the conduction bandedge  $E_c$

$$E^- = E_c - 0.57 \text{ eV} \quad [2]$$

$$E^{=} = E_c - 0.11 \text{ eV} \quad [3]$$

as the bandgap narrows with increasing temperature

$$E_G = E_c - E_v = 1.17 - 4.73 \times 10^{-4} \left( \frac{T^2}{T + 636} \right) \quad [4]$$

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

$$C^+ : C^- : C^{=} = \exp \frac{E^+ - E_F}{kT} : 1 : \exp \frac{E_F - E^-}{kT} : \exp \frac{2E_F - E^- - E^{=}}{kT} \quad [5]$$

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

$$C^T = 1 + \exp \frac{E^+ - E_F}{kT} + \exp \frac{E_F - E^-}{kT} + \exp \frac{2E_F - E^- - E^{=}}{kT} \quad [6]$$

By the use of Boltzmann approximation

$$\exp \frac{E_i - E_F}{kT} = \frac{p}{n_i} \quad [7]$$

where  $E_i$  is the intrinsic Fermi level

$$E_i = \frac{F_G}{2} - \frac{kT}{4} \quad [8]$$

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

$$n_i = 3.87 \times 10^{16} T^{3/2} \exp \left( - \frac{0.605}{kT} \right) \quad [9]$$

Equation [6] can be expressed as

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

where

$$\beta^+ = \exp \frac{E^+ - E_i}{kT}$$

$$\beta^- = \exp \frac{E_i - E^-}{kT} \quad [11]$$

and

$$\beta^{=} = \exp \frac{2E_i - E^- - E^{=}}{kT}$$

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

$$\frac{D}{D_i} = \frac{1 + \beta^+ \left( \frac{p}{n_i} \right) + \beta^- \left( \frac{n_i}{p} \right) + \beta^{=} \left( \frac{n_i}{p} \right)^2}{1 + \beta^+ + \beta^- + \beta^{=}} \quad [12]$$

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

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

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

$$\frac{\partial N}{\partial y} = \frac{\partial}{\partial y} \left( D \frac{\partial N}{\partial t} \right) \quad [14]$$

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

$$y = y_j = j\Delta y \quad j = \dots, -2, -1, 0, 1, 2, \dots$$

$$t = t_i = i\Delta t \quad i = 0, 1, 2, \dots$$

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

$$N(y_j, t_{i+1}) = M [D(y_{j+1}, t_i) N(y_{j+1}, t_i) + D(y_{j-1}, t_i) N(y_{j-1}, t_i)] + [1 - 2MD(y_j, t_i)] N(y_j, t_i) \quad [15]$$

where  $M = \Delta t / (\Delta y)^2$  is called the mesh ratio and  $D(y_j, t_i)$  is evaluated from Eq. [12] by letting  $p = N(y_j, t_i)$  for  $N(y_j, t_i) > n_i$  and  $p = n_i$  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  $M$  of  $1/4 D_0$ , a space interval  $\Delta y$  of  $\sqrt{4D_0 t}/10$ , and a time interval  $\Delta t$  of  $t/100$  are chosen.

The calculated profiles of  $N/N_0$  vs.  $y/\sqrt{4D_0 t}$  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

$$\frac{N}{N_0} = 1 - 0.631 \left( \frac{y}{\sqrt{4D_0 t}} \right) - 0.214 \left( \frac{y}{\sqrt{4D_0 t}} \right)^2 \quad [16]$$

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  $\sqrt{4D_0 t}$ .

### Results and Discussion

The experimental result of sheet resistance as a function of deposition time at various temperatures are

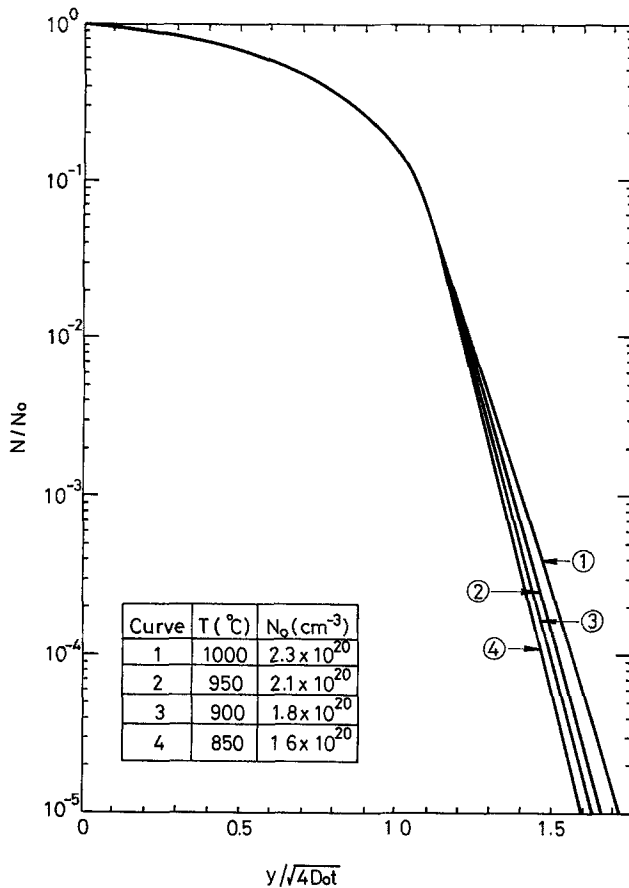


Fig. 2. Normalized profiles of  $N/N_0$  vs.  $y/\sqrt{4D_0t}$  for various temperatures.

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

$$R_s^{-1} = \int q\mu_p N dy \quad [17]$$

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

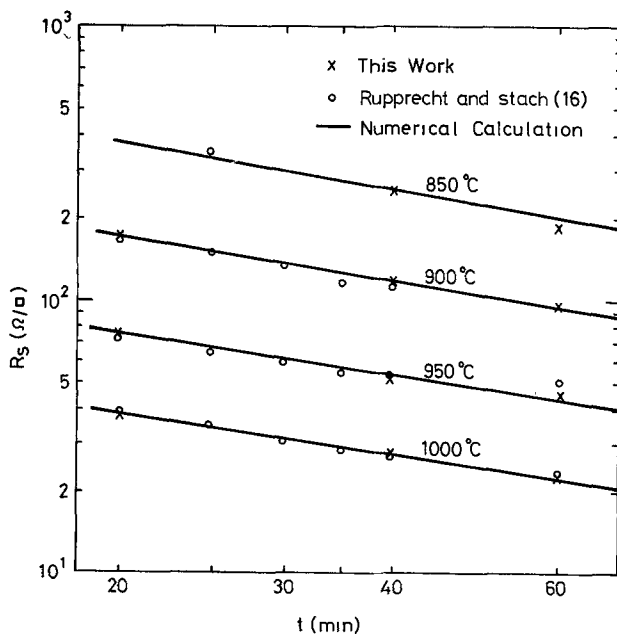


Fig. 3. Sheet resistance vs. deposition time for several temperatures.

$$\mu_p = 49.7 + \frac{418}{1 + (N/1.6 \times 10^{17})^{0.7}} \quad [18]$$

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

$$R_s^{-1} = q\bar{\mu}_p Q \quad [19]$$

where  $\bar{\mu}_p$  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  $\bar{\mu}_p \approx 54 \text{ cm}^2/\text{Vsec}$  for  $N_0 \approx 2 \times 10^{20} \text{ cm}^{-3}$  and  $Q \approx 0.628 N_0 \sqrt{4D_0t}$  for all deposited temperatures used in this work. Therefore, the sheet resistance expression [19] becomes

$$R_s = 9.2 \times 10^{16}/N_0 \sqrt{D_0t} \Omega/\text{sq} \quad [20]$$

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  $10^{-2}$  in Fig. 2, then

$$y_j \approx 2.4 \sqrt{D_0t} \quad [21]$$

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  $\text{BBr}_3$  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  $\text{BBr}_3$  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

$$\frac{p}{N} = e^{\Delta} \quad [22]$$

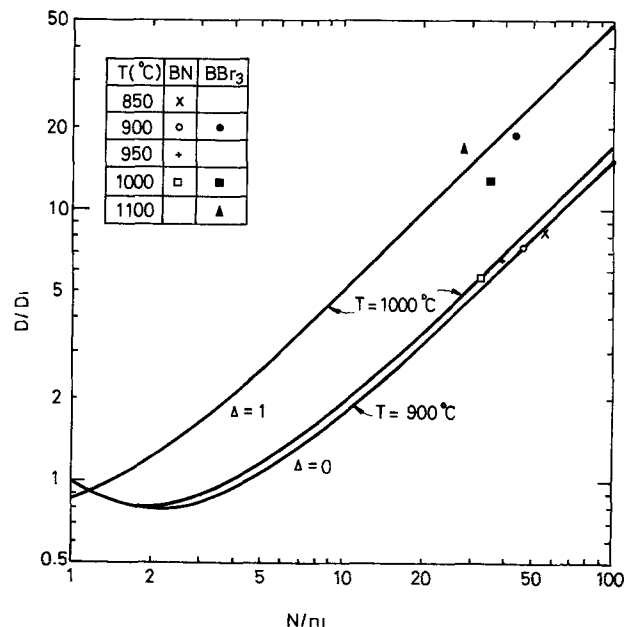


Fig. 4. Normalized diffusivity vs. normalized boron concentration under different conditions.

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

$$\frac{D}{D_i(0)} = \frac{1 + \beta^+ e^{\Delta} \left(\frac{N}{n_i}\right) + \beta^- e^{-\Delta} \left(\frac{N}{n_i}\right)^{-1} + \beta^= e^{-2\Delta} \left(\frac{N}{n_i}\right)^{-2}}{1 + \beta^+ + \beta^- + \beta^=} \quad [23]$$

where  $D_i(0)$  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  $BBr_3$  source deposition.

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

$$\frac{D_i(\Delta)}{D_i(0)} = \frac{1 + \beta^+ e^{\Delta} + \beta^- e^{-\Delta} + \beta^= e^{-2\Delta}}{1 + \beta^+ + \beta^- + \beta^=} \quad [24]$$

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 ex-

plained 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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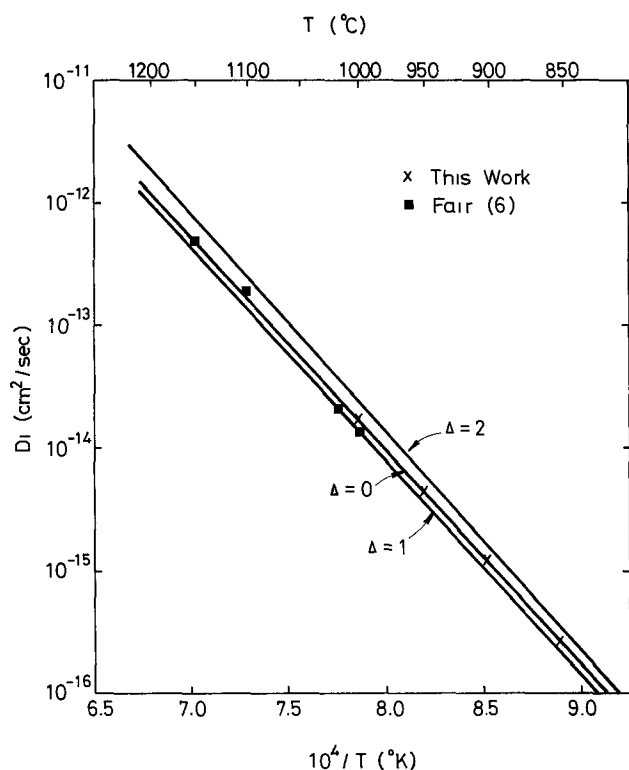


Fig. 5. Intrinsic diffusivity of boron in silicon with and without band bending.