The Effect of Trace Amounts of Water Vapor on Boron Doping in Epitaxially Grown Silicon

J. Bloem*

Semiconductor Development Laboratory, N. V. Philips Gloeilampenfabrieken, Nijmegen, Holland

ABSTRACT

It was found that silicon epitaxy from silane (SiH_4) can tolerate unexpectedly high water concentrations in the gas phase before deterioration of the growing layer sets in. The extent of boron doping from B_2H_6, however, is shown to be strongly influenced by water vapor concentrations in the ppm region. It is shown that HCl gas at partial pressures greater than 10^{-3} atm has a similar influence on the extent of boron doping and that it makes the system less susceptible to small variations in water vapor concentrations. The results can be explained by consideration of the various gas phase equilibria at or near the silicon-gas interface.

In the epitaxial growth of silicon layers it was discovered early that the presence of oxygen or water vapor has a detrimental effect on the quality of the epitaxial layers (1). In doping the silicon layers, boron doping (using B_2H_6 as the doping agent) appeared to be a more difficult operation than doping with P, As, or Sb compounds. The water content of a well-purified gas was seen to lie in the order of 1 ppm or less (10^{-6} atm in the 1 atm open-tube system used); this value is orders of magnitude higher than the B_2H_6 concentration of 10^{-10} atm used in doping. Because the varying results in boron doping were thought to be explained by small differences in the efficiency of the gas purification, by small leaks in the gas-handling system, or by residual moisture on the surface of the quartz reactor, it seemed appropriate to study the effect of trace amounts of water vapor on boron incorporation.

Experimental Procedure

The horizontal, air-cooled epitaxial reactor consisted of a quartz tube 80 cm in length, of rectangular cross section (10×2.5 cm^2) into which a SiC-coated graphite susceptor ($9.5 \times 24 \times 1.0$ cm^3) was placed. The susceptor was loaded with 10 silicon slices of 38 mm diam in two parallel rows and was R.F.-heated. The main gas stream for all runs was 75 liters hydrogen per min. The silicon substrates were (111)-oriented, mechanically and chemically polished, with dislocation densities less than 500 dislocations per cm^2. The surface quality of the slices was such that under normal conditions a heat treatment prior to epitaxial growth of the slices in hydrogen at 1250°C for 15 min was sufficient to obtain layers free of spikes and stacking faults. The resistivities of the epitaxial layers were measured both by the four-point probe technique (2) on reference slices of opposite resistivity types and by spreading resistance measurements (3). When p-type doping was studied, higher resistivity (about 2 ohm-cm) n-type substrates were placed on the susceptor along with the low-resistivity (0.007 ohm-cm) n-type substrates. It appeared that lower resistivities were the same on both types of substrates within the experimental error (±15%). By tilting the susceptor (1°30′) and slightly adjusting the temperature over the susceptor (leading edge about 20° cooler than end section), depletion of the gas phase was counteracted in such a way that both thickness and resistivity variations were minimized (±5% for thickness, ±15% for resistivity). Thickness and resistivity values on slices 4 and 10 cm from the leading edge were taken to be representative for the run.

The thickness of the grown layers was measured by the infrared interference technique (4). For the thickness measurements layers grown on Sb-doped substrates (resistivity 0.007 ohm-cm) were used. The thickness of the epitaxial layers was monitored from 10 to 20 μm. Unless otherwise stated, the silicon growth rate was kept at about 1 μ/min ($p_{SiH_4} = 10^{-3}$ atm). The values from the *IR* interference technique were in accord with those obtained by the bevel and stain method. The temperature of the substrates was measured with an optical pyrometer, and the readings were corrected for the emissivity of silicon (5).

The starting silane and diborane (4% SiH_4 in H_2, 1% B_2H_6 in H_2) were diluted with hydrogen to the wanted partial pressures using calibrated flowmeters. The water vapor was obtained from an evaporation cell filled with water at constant temperature (20°C). By passing a small hydrogen stream (0-100 cm^3) over the surface of the liquid and mixing this with the main gas stream (75 liters/min) the water vapor concentration in H_2 was varied from 0 to 50 ppm ($0\text{-}50 \times 10^{-6}$ atm). In separate runs analysis with a Beckmann moisture meter showed the measured water content of the gas to be in good agreement with the amount calculated from the vapor pressure of water. Epitaxial runs without diborane doping were performed, and silicon layer resistivities higher than 20 ohm-cm, n-type, were consistently obtained. On the addition of water vapor the resistivity remained on this level. Prolonged annealing of the layers at 500°C shows the donor activity expected from the oxygen content (6). The addition of HCl showed the resistivity to decrease; for the highest HCl concentration (2×10^{-2} atm) the resistivity dropped to 3 ohm-cm (1.6×10^{15} donors/cm^3). Where necessary, corrections for this additional doping effect were applied.

Experimental Results

Influence of water vapor on silicon epitaxy.—Epitaxial runs at 1150°C with increasing amounts of water vapor showed that up to 40×10^{-6} atm of water vapor in the gas did not cause stacking faults in the layers, provided that the slices were preheated for 15 min in hydrogen at 1250°C before the introduction of silane. For $p_{H_2O} \approx 10 \times 10^{-6}$ atm small pits become visible on the Si surface. This is an aftergrowth effect: when the silane flow is terminated the freshly grown layer is etched slightly by the water vapor present in the hydrogen. On further cooling, the formation of SiO_2 could be expected; this is not observed presumably because the cooling period is too short. For values of p_{H_2O} greater than 10×10^{-6} atm the onset of gas phase reactions gave a brown deposit on the relatively cold upper wall of the reactor. This deposit was accompanied by a decrease in epitaxial layer thickness; the farther the substrate from the leading edge of the susceptor, the greater the decrease. With $p_{H_2O} = 40 \times$

* Electrochemical Society Active Member.
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10^{-6} atm, deposition of silicon was present only on the first row of silicon slices.

Influence of water vapor on boron doping.—In order to examine the boron content of the grown layers as a function of the silicon growth rate, the partial pressure of diborane ($p_{B_2H_6}$) was kept constant whereas p_{SiH_4} and consequently the growth rate was varied. The variation of growth rate with p_{SiH_4} is shown in Fig. 1, and the boron concentration as a function of growth rate is depicted in Fig. 2. The scatter in the results shown in Fig. 2 decreased considerably after checking the apparatus for minor leaks and careful drying of the quartz tube used. Subsequent experiments then showed the same behavior, *i.e.* no distinct increase or decrease of the concentration of boron incorporated in the layers as long as $p_{B_2H_6}$ is kept constant; only for the highest growth rates a slight decrease in boron concentration is found.

The boron concentration in the layers varies linearly with $p_{B_2H_6}$ (Fig. 3). If the water vapor pressure is increased for a fixed value of $p_{B_2H_6}$ and p_{SiH_4}, a decreasing boron concentration is found; this effect occurs for various diborane concentrations (Fig. 4). For higher values of p_{H_2O} the decrease is proportional to $(p_{H_2O})^2$ (Fig. 4).

The boron concentration in the epitaxial layers is temperature dependent; contrary to the findings for n-type dopants (7) the concentration increases with increasing temperature (Fig. 5). There is some indication of a decreasing influence of water with increasing temperature.

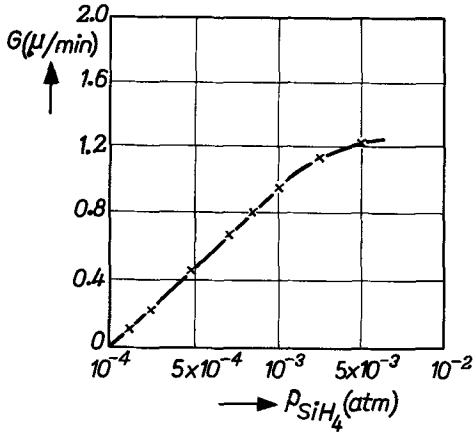

Fig. 1. Growth rate of silicon as a function of the partial pressure of silane in the gas phase.

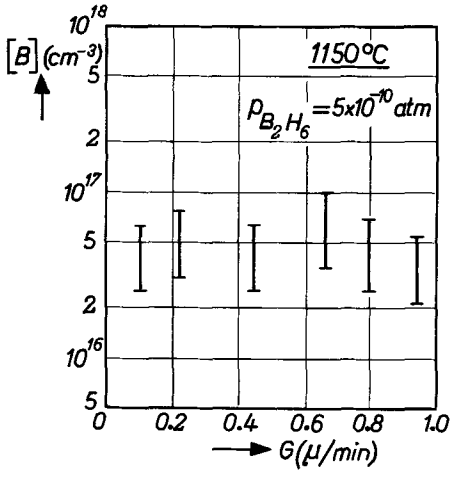

Fig. 2. Boron concentration in the epitaxial layers as a function of silicon growth rate (constant partial pressure of diborane in the system).

Influence of HCl on boron doping.—The introduction of HCl in the epitaxial reactor shows only a small influence on silicon growth rate (8): a ratio p_{HCl}/p_{SiH_4} of 1 reduces the silicon growth rate by 0.4% and a ratio of 4 gives a reduction of 6%. The presence of HCl also counteracts the incorporation of boron in the growing silicon (9).[1] The influence of the introduction of HCl on the acceptor concentration is pronounced if no water vapor is added (Fig. 6, curve $p_{H_2O} = 0$). For an HCl concentration greater than 10^{-3} atm (p_{HCl}/

[1] This effect is used in obtaining pure polycrystalline silicon by the pyrolysis of chlorosilanes.

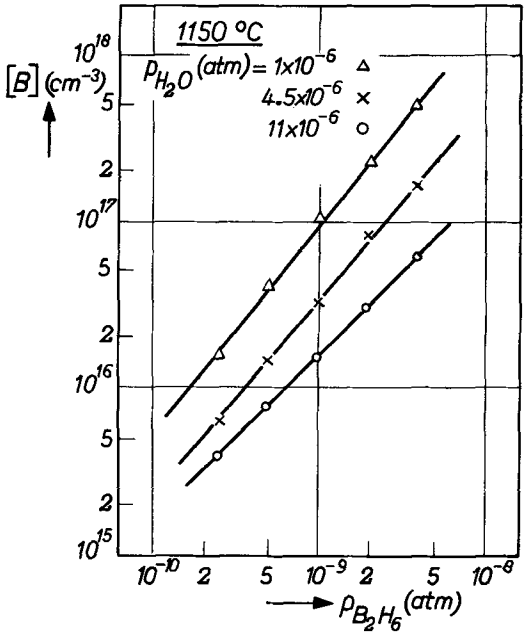

Fig. 3. Boron concentration in epitaxially grown layers vs. the diborane partial pressure introduced into the reactor.

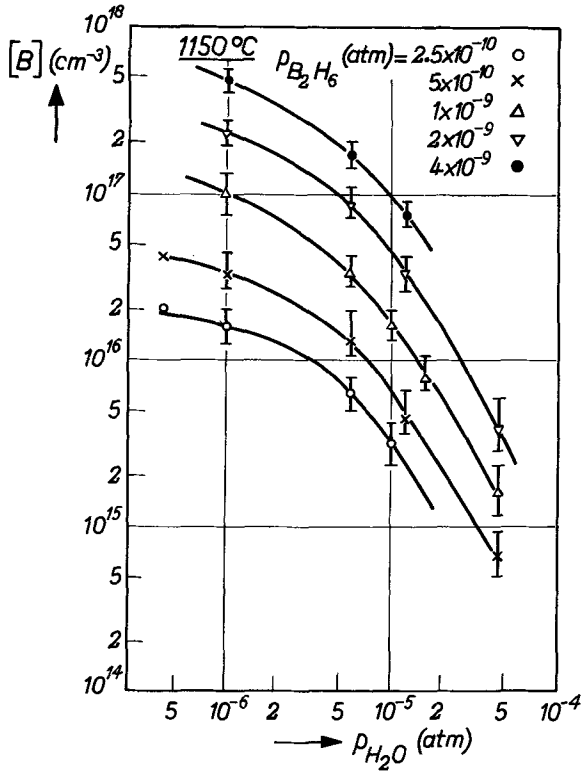

Fig. 4. Variation of boron concentration in the epitaxial silicon layers with water vapor pressure in the gas.

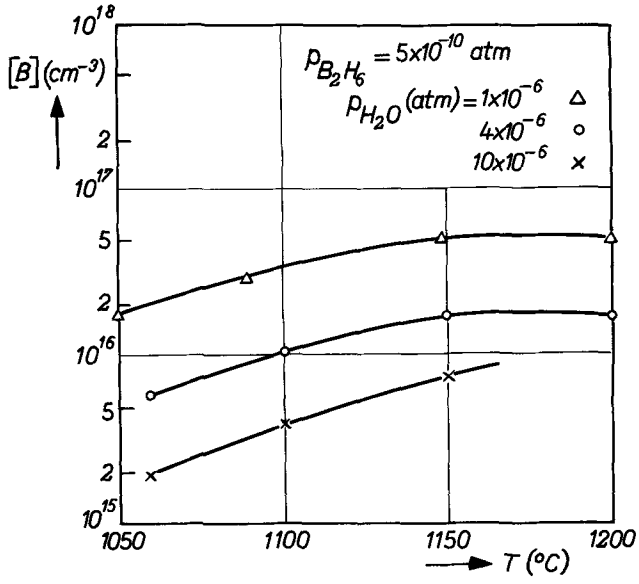

Fig. 5. Temperature dependence of the boron concentration in epitaxial layers for a constant diborane concentration and various water vapor partial pressure in the gas.

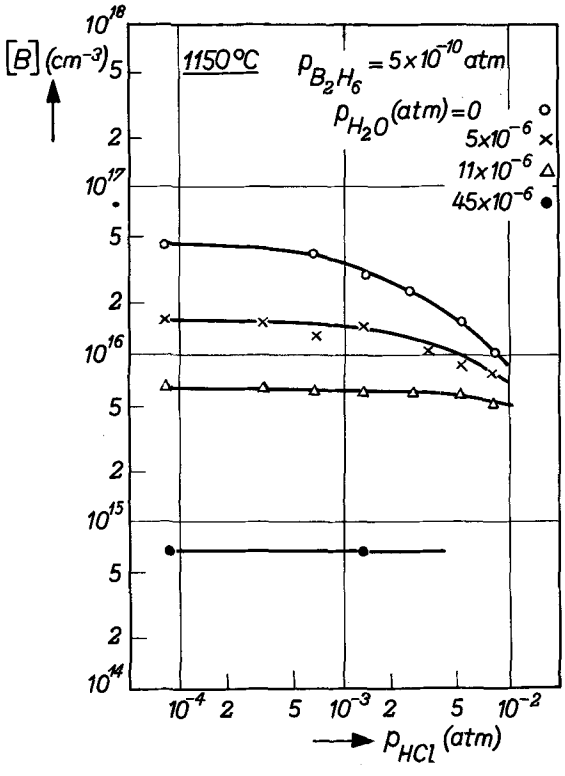

Fig. 6. Boron concentration in epitaxial silicon as a function of the amount of hydrochloric acid added in the gas phase, with the water vapor content as parameter.

$p_{SiH_4} = 1$) the boron concentration in the grown layers is seen to decrease with p_{HCl}.

For gas mixtures containing H_2O, HCl, B_2H_6, and SiH_4 in hydrogen the result is depicted in Fig. 6 and 7. At low values of p_{HCl} the influence of water vapor is more pronounced than at higher values of p_{HCl}.

Discussion

In this section the influence of water and hydrochloric acid vapor on the silicon growth rate and on the boron doping will be treated, starting from possible

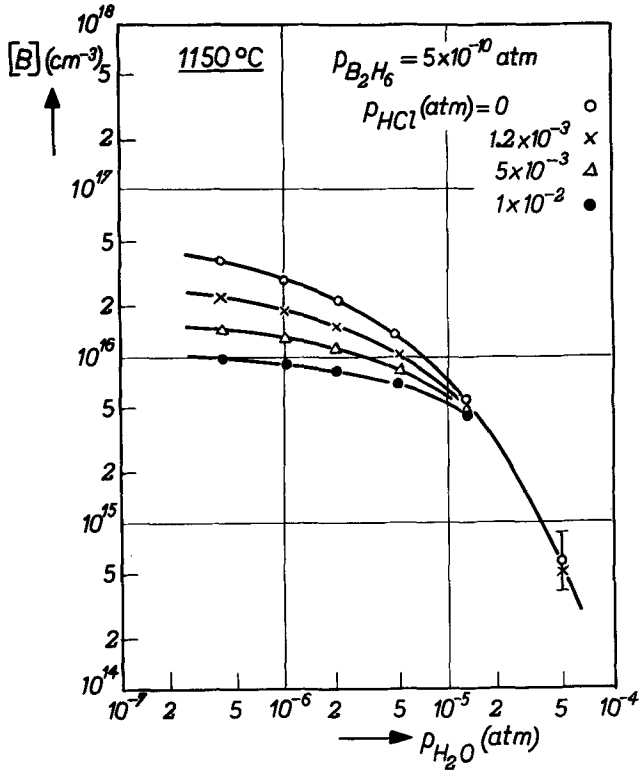

Fig. 7. Boron concentration in epitaxial silicon for a constant vapor pressure of diborane vs. the water vapor pressure, with the hydrochloric acid content as parameter.

reactions in the gas-phase and at the gas-silicon interface. From existing thermochemical data the predominant reaction products can be inferred, the main object being to relate the variation of the boron concentration in silicon to the variations in the gas phase composition. It will be assumed that the reactions are surface catalyzed, *i.e.* the reactions are thought to proceed to equilibrium, the equilibrium constants not being altered by the presence of the surface.

Influence of water vapor on silicon epitaxy.—Two reactions on the silicon surface are of importance, *viz.*

$$Si_{(s)} + 2H_2O_{(g)} = SiO_{2(s)} + 2H_{2(g)}$$
$$K_1 = (p_{H_2O})^{-2} \text{ for } p_{H_2} = 1 \quad [1]$$

$$Si_{(s)} + SiO_{2(s)} = 2\,SiO_{(g)}$$
$$K_2 = (p_{SiO})^2 \quad [2]$$

and the combination of [1] and [2]

$$Si_{(s)} + H_2O_{(g)} = SiO_{(g)} + H_{2(g)}$$
$$K_3 = p_{SiO}/p_{H_2O} \quad [3]$$

If equilibrium [3] at the silicon surface is reached sufficiently rapidly, the value of K_3 being about 30 at 1400°K (10), then the equilibrium vapor pressure of water near the surface will be lower than in the main gas phase. For a diffusion-controlled reaction rate the water vapor pressure at the surface is reduced by a factor K_3, assuming the diffusion coefficients of H_2O and SiO to be the same. In Fig. 8 water and SiO vapor pressures according to Eq [1] and [2] are given (10), *i.e.* values of $K_1^{-1/2}$ and $K_2^{1/2}$ as a function of temperature for $p_{H_2} = 1$. In the regions II and III, formation of SiO_2 is expected (Eq. [1]); whereas in region I the silicon surface will be free from surface oxides. In region II, however, the SiO_2 formed on the surface reacts with silicon to form volatile SiO (Eq. [2]) and the value of p_{H_2O} at the surface is reduced below the value corresponding to the lower curve in Fig. 8 at the temperature studied. It is only for water vapor pressures higher than the value on the upper curve ($K_2^{1/2}$) that the whole surface will be covered by SiO_2, that

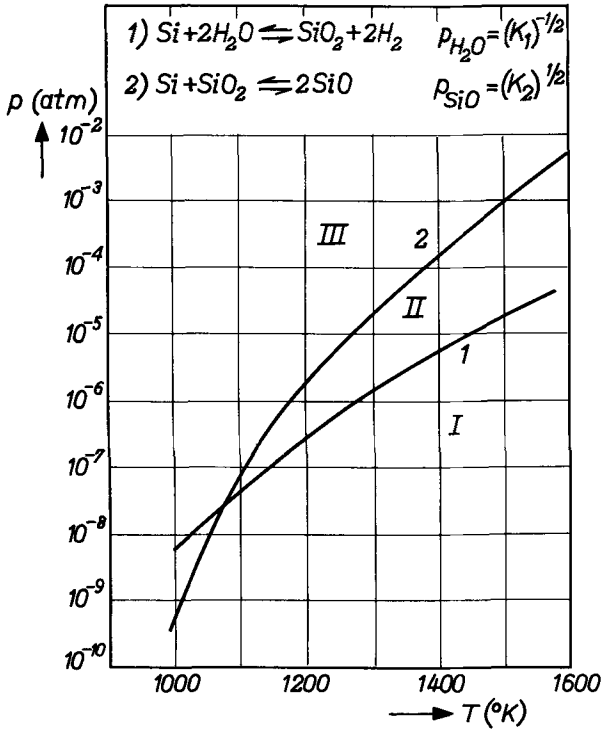

Fig. 8. Water vapor pressures that can be allowed in the gas phase growing epitaxial silicon layers. Curve 1 gives the water vapor pressures at the silicon surface in equilibrium with solid silicon dioxide as a function of temperature. Curve 2 gives the vapor pressure of silicon monoxide in equilibrium with solid silicon and silicon dioxide. For water vapor pressures in region II the formation of volatile SiO prevents the formation of solid SiO_2 on the silicon surface.

is, the actual water vapor pressure at the surface then has reached the critical value indicated by the lower curve. From reaction [1] it would be expected that at 1400°K water vapor pressures greater than 4 ppm would cause the formation of SiO_2. In practice, with up to 50 ppm no deterioration of the layers was observed because of reaction [2]. Epitaxy becomes impossible, however, because of another reason, *i.e.* excessive gas phase reactions.

Water vapor can react with silane in the gas phase or etch the silicon surface. In both cases gaseous SiO is formed. It is postulated that this SiO diffuses into colder parts of the gas stream and decomposes according to

$$2SiO = Si + SiO_2$$

As the vapor pressures of Si and SiO_2 are low, the gas phase is easily supersaturated giving rise to gas phase nucleation of the corresponding compounds. Subsequently decomposition of SiH_4 occurs on the solid nuclei leading to a serious depletion of silane in the gas phase.

Boron doping.—In Fig. 2 it is shown that the boron concentration in the epitaxial layers does not depend on the silicon growth rate under the prevailing conditions.

The silicon growth rate is diffusion-controlled in the range of temperatures studied (8), but for the incorporation of boron in the growing layer diffusion control is not indicated, because otherwise increasing growth rates due to increasing concentrations of SiH_4 would give a decreasing boron concentration. The same number of boron atoms has to be incorporated in increasingly thicker silicon layers.

B_2H_6 is reported to decompose rapidly at elevated temperatures into BH_2 (11) and BH_3 (12). This explains the slope of the curve in Fig. 3, which is about unity. If B_2H_6 were stable, a slope of 0.5 would be expected. The incorporation of boron in silicon can be given as

$$B_2H_6 = 2BH_3(g) \qquad K_4 = 7.0 \quad \text{at } 1400°K \text{ (13)} \qquad [4]$$

$$BH_3(g) = B(g) + 3/2\ H_2(g) \qquad K_5 = 3.2 \times 10^{-8} \quad \text{at } 1400°K \text{ (13)} \qquad [5]$$

$$B(g) = B_{Si} \qquad K_6 \qquad [6]$$

$$B_{Si} = B^-_{Si} + p \qquad K_7 \qquad [7]$$

The gas phase segregation coefficient of boron is best defined as the equilibrium constant of the reaction describing the incorporation of elemental boron in silicon giving ionized acceptor centers.[2]

$$\gamma_B = \frac{p_B}{[B^-]_{Si}} = \frac{p}{K_6K_7} = \frac{n_i}{K_6K_7} \qquad [8]$$

As the acceptor may be assumed to be fully ionized, and the value of p is equal to the intrinsic carrier concentration, n_i at the temperature of the experiment, for B concentrations well below n_i (approximately 10^{20} cm^{-3} at 1400°K or $2 \cdot 10^{-3}$ acceptors per Si atom), K_7 is a constant giving the number density of states in the valence band of silicon. As the ambient pressure is unity, p_B in Eq. [8] is equal to the mole ratio of boron in the gas phase close to the silicon surface. The concentration of acceptor centers in silicon will further be denoted by the symbol [B].

A practical segregation coefficient relates the concentration of dopant in the system ($p_{B_2H_6} = p_o$) to the resulting acceptor concentration in the grown layer. With Eq. [4]-[7] we find, in the absence of water or HCl

$$\gamma_{B_2H_6} = \frac{p_o}{[B]} = \frac{1}{2}\gamma_{BH_3} = \frac{1}{2K_5}\gamma_B \qquad [9]$$

In the gas phase B_2H_6 is dissociated completely into BH_3, and therefore $p_{BH_3} = 2\,p_o$.

Influence of water and HCl concentration on doping.—If water vapor and HCl are present in the gas phase, then reactions with the highly reactive boron hydrides can be expected. According to thermodynamic data (13), the most probable reaction products are BHO_2, BCl, and BClO.

$$BH_3 + 2H_2O = BHO_2 + 3H_2 \qquad K_{10} = 2 \times 10^{11} \quad \text{at } 1400°K \qquad [10]$$

$$BH_3 + HCl = BCl + 2H_2 \qquad K_{11} = 20 \quad \text{at } 1400°K \qquad [11]$$

$$BCl + H_2O = BClO + H_2 \qquad K_{12} = 1.5 \times 10^6 \quad \text{at } 1400°K \qquad [12]$$

from [10] and [11] we obtain

$$H_2 + HBO_2 + HCl = BCl + 2H_2O \qquad K_{13} = 10^{-10} \qquad [13]$$

moreover

$$2\,p_o = p_{BH_3} + p_B + p_{BHO_2} + p_{BClO} + p_{BCl} \qquad [14]$$

With Eq. [1]-[14] the resulting equilibrium can be estimated for any initial gas composition. As all equilibria are coupled it is sufficient to take one boron compound as the source of elemental boron in order to obtain the amount of boron incorporated in the growing layers. It is convenient to select BH_3. According to Brouwer (14), simple linear relations are obtained by splitting Eq. [14] into a number of limiting cases; *e.g.*

[2] The segregation coefficient is often defined as $\alpha = \left(\frac{B}{Si}\right)_{gas} / \left(\frac{B}{Si}\right)_{solid}$. This definition is only meaningful if B and Si are incorporated in the same manner; otherwise α depends on the value of p_{SiH_4} and thus on the silicon growth rate.

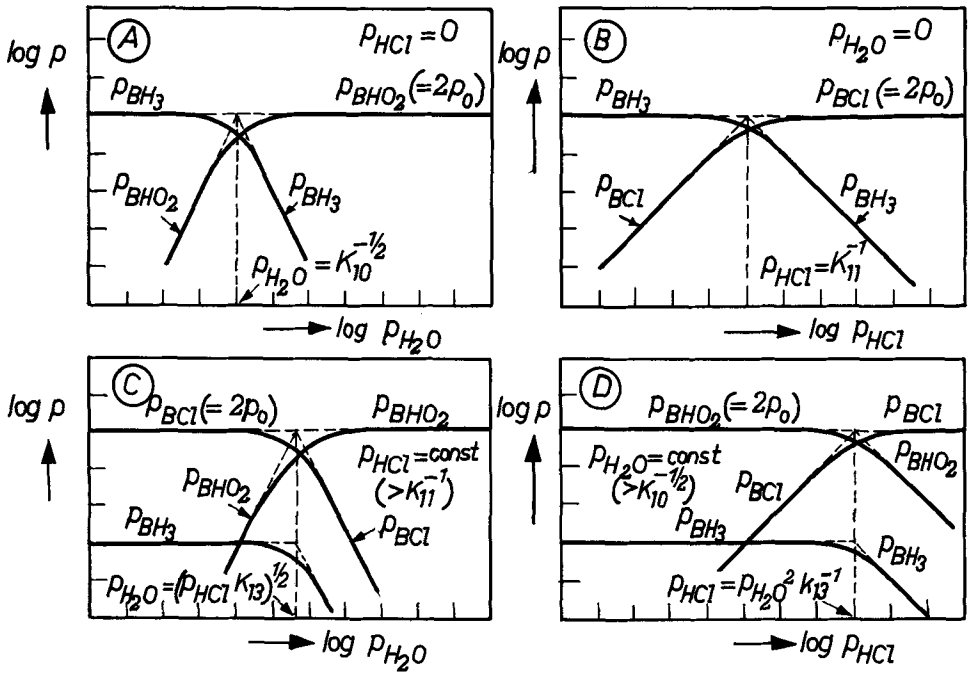

Fig. 9. Schematic representation of the variation of the partial pressures of boron compounds in the gas phase as a function of the water and/or hydrochloric acid content of the gas: A = variation with p_{H_2O} for p_{HCl} = 0, B = variation with p_{HCl} for p_{H_2O} = 0, C = variation with p_{H_2O} for p_{HCl} = constant ($> K_{11}^{-1}$), and D = variation with p_{HCl} for p_{H_2O} = constant ($> K_{10}^{-1/2}$).

$2p_o = p_{BH_3}$; $2p_o = p_{BHO_2}$ in the presence of water or $2p_o = p_{BCl}$ if sufficient HCl is present. In doing this and introducing the values in Eq. [10]-[13] the interrelations can be depicted as in Fig. 9. The acceptor concentration in silicon is proportional to the value of p_{BH_3}. In Fig. 9c and 9d it is seen that p_{BH_3} is constant for not too great values of p_{H_2O} or p_{HCl}. If BClO would be present in greater concentrations and a region $2p_o = p_{BClO}$ would appear, then in Fig. 9c the value of p_{BH_3} would be decreasing with p_{H_2O} even in the low-water vapor concentration range. As this is not apparent in Fig. 7, it is expected that the value of K_{12} has to be lower than calculated. In order to bring the calculated and experimental results into accord, the value of K_{10} and K_{11} have to be taken higher than given with Eq. [10] and [11] together with a lower value of K_{12}. These corrections are well within the accuracy of the thermochemical data (*e.g.* heat of formation of BH_3 given as 25.5 ± 10 kcal mole^{-1} (12) for BH_2 as 48 ± 15 kcal mole^{-1} (13).) In total we expect

$$p_{BH_3} = \frac{2p_o}{1 + K_{10}p_{H_2O}^2 + K_{11}p_{HCl}} \qquad [15]$$

By definition, $\gamma_{BH_3} = p_{BH_3}/[B]$; also, the actual water vapor pressure at the interface is lower than in the main gas by a factor K_3. p_{HCl}, however, will have the same value at the interface and in the main gas (8). Therefore

$$[B] = \frac{2p_o}{\gamma_{BH_3}\left\{1 + K_{10}\left(\frac{p_{H_2O}}{K_3}\right)^2 + K_{11}p_{HCl}\right\}} \qquad [16]$$

The value of [B] can be transformed into a concentration per cm^3 by multiplication with 5×10^{22}, the number of atoms per cm^3 of silicon. The experiments at 1150°C can then be explained with $\gamma_{BH_3} = 10^{-3}$, $K_{10} = 2 \times 10^{13}$, $K_3 = 30$, $K_{11} = 10^3$; with Eq. [9] we find $\gamma_{B_2H_6} = 5 \times 10^{-4}$.

In conclusion it can be stated that the influence of varying amounts of water vapor and HCl in the gas phase on the boron concentration in the silicon can be explained semiquantitatively by assuming the gas phase reactions to come to equilibrium at the silicon interface. The main features of the experimental results are in accord with the predictions given in Fig. 9.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1972 JOURNAL.

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