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Citation: *J. Appl. Phys.* **74**, 6094 (1993); doi: 10.1063/1.355171

View online: <http://dx.doi.org/10.1063/1.355171>

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# Effects of Si incorporation on the structural change of $a\text{-B}_x\text{Si}_{1-x}$ alloy films

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(Received 19 January 1993; accepted for publication 31 July 1993)

Amorphous  $\text{B}_x\text{Si}_{1-x}$  films can be easily prepared by low-pressure chemical vapor deposition over the whole range of  $x$  from 0 to 1. In this article, the structural change of  $\text{B}_x\text{Si}_{1-x}$  films ( $0 < x < 1$ ) was studied by x-ray diffraction and infrared (IR) absorption experiments. It was found that these two methods are complementary to each other. X-ray results showed that when  $x$  is decreased, there is a gradual transition from the  $a\text{-B}$  structure, through the  $\text{SiB}_4$  structure, to the amorphous silicon structure. The transition to  $a\text{-Si}$  structure is complete at a surprisingly high boron concentration of around 40 at. %. Infrared data also revealed an unexpected result—that the presence of boron suppresses the formation of Si—H types of bonds in high silicon content films, in strong contrast to films prepared by the glow discharge method. Another interesting feature of the IR absorption spectra is the predominance of an absorption band, related to the presence of boronlike icosahedral clusters, in all films with boron concentration to as low as 17.6 at. %. Such clusters may be responsible for the easy formation of an impurity band lying about 0.2 eV above the valence mobility edge, as observed by transport measurements of boron-doped  $a\text{-Si}$  films prepared by low-pressure chemical vapor deposition.

## I. INTRODUCTION

In a recent study on the transport properties of amorphous silicon-boron films prepared by low-pressure chemical vapor deposition (LPCVD),<sup>1</sup> it was found that the band tail of these films is narrower than corresponding films prepared by the glow discharge method. Thus boron-doped LPCVD  $a\text{-Si:H}$  can have a higher electrical conductivity than the glow-discharge films. However, it was also found that boron can be easily incorporated into the silicon matrix at high solid phase concentration in the LPCVD method, leading to the formation of an impurity band situated about 0.2 eV above  $E_v$ , limiting the position of Fermi level  $E_F - E_v$  to no less than 0.25 eV. If the formation of such an impurity band can be suppressed, the LPCVD method will provide an excellent way of efficiently producing  $p$ -doped  $a\text{-Si:H}$  films. To do this, one should first get a better understanding why such an impurity band forms in LPCVD films.

In this article, the preparation condition of  $a\text{-B}_x\text{Si}_{1-x}$  will be scanned through a wide range of substrate temperatures  $T_s$  and an  $x$  value from 0 to 1. It is hoped that the structural change of the films as  $T_s$  and  $x$  are varied can be followed, and some correlation to the aforementioned impurity band may be found.

## II. SAMPLE PREPARATION

The LPCVD reactor consists of a graphite susceptor placed inside a quartz tube whereby the reactant gases are fed into the tube at one end and are pumped off at the other end by a rotary pump with pumping speed controlled by an adjustable butterfly valve. A diffusion pump is also connected to the system so that the reactor can be pumped

down to  $1 \times 10^{-6}$  Torr and subsequently purged by ultra-high purity nitrogen gas prior to admitting reactant gases for film deposition. The flow rates of the reactant gases are controlled by individual mass flow controllers. The substrate temperature is controlled by a specially designed induction heater, described in detail elsewhere,<sup>2</sup> and can be set at any value between room temperature and 800 °C. The substrates used were either 7059 glass slides (for x-ray experiments) or  $p$ -type silicon wafers (for infrared absorption experiments).  $a\text{-B}_x\text{Si}_{1-x}$  films with  $x$  between 0 and 1 were then prepared by thermal decomposition with a mixture of 10%  $\text{SiH}_4$  balanced in hydrogen and 5%  $\text{B}_2\text{H}_6$  balanced in argon through a variation of the gas flow rate ratio  $R = (\text{B}_2\text{H}_6)/(\text{SiH}_4)$ . The reactor pressure during deposition was kept between 10 mTorr and 5 Torr.

The coating rate (CR) depends sensitively on the substrate temperature  $T_s$ , the reactor pressure  $p$ , and gas flow rate ratio  $R$ . In general, CR increases with increasing  $T_s$  and  $R$ . Thus the highest CR is recorded for pure boron film deposition. Typical CR for  $T_s = 620$  °C,  $p = 1$  Torr, and  $(\text{B}_2\text{H}_6) = 1$  sccm is 24 Å/s for pure boron and is less than 5 Å/s when  $R = 5 \times 10^{-3}$  [ $(\text{B}_2\text{H}_6) = 3 \times 10^{-2}$  sccm and  $(\text{SiH}_4) = 6$  sccm]. At  $T_s = 300$  °C and  $p = 5$  Torr, CR is  $\sim 2$  Å/s for pure boron and is less than 0.1 Å/s for  $R = 5 \times 10^{-3}$ .

In order to study how the incorporation of silicon atoms can affect the properties of  $a\text{-B}_x\text{Si}_{1-x}$  samples with a wide range of  $x$  were prepared. Since  $x$  can depend both on  $T_s$  and  $R$ , three series of samples were deposited at  $T_s = 300, 460,$  and  $620$  °C with  $R$  ranging from  $5 \times 10^{-3}$  to 5. Series of boron films were also prepared under similar conditions for comparison. Boron concentrations of the

TABLE I. Boron concentration  $x$  of  $B_xSi_{1-x}$  films deposited at 460 and 620 °C.

$T_s$ (°C) \ $R$	$5 \times 10^0$	$5 \times 10^{-1}$	$5 \times 10^{-2}$	$5 \times 10^{-3}$
460	0.87	0.71	0.51	0.18
620	0.92	0.77	0.43	0.09

films were determined by energy dispersive x-ray spectroscopy (EDX) and the results are listed in Table I.

### III. EXPERIMENT DETAILS

Since our samples are mostly amorphous, qualitative information about structural changes of the films as a function of  $x$  and  $T_s$  can be most conveniently obtained by taking Debye-Scherrer x-ray diffraction patterns using the transmission technique. For this purpose, the glass substrates were first removed by hydrofluoric acid and about 20 pieces of unsupported films were piled up to get a total thickness of about 0.1 mm. This thickness is close to the value required for a transmission experiment according to Cullity.<sup>3</sup>

Films coated on Si wafers were used in IR absorption experiments that were conducted in a conventional double beam spectrophotometer in a range from 500 to 4000  $\text{cm}^{-1}$ . Interference can occur if the film thickness is comparable to the wavelength of light in the sample. Care should be taken to differentiate between the true absorption bands and the interference effect.

### IV. PURE BORON FILMS

The x-ray diffraction patterns of boron films prepared at  $T_s$  between 300 and 800 °C are all similar and show that all these films are amorphous. The pattern consists of four broad halos to which the following bands of  $d$  spacings can be assigned: halo I (strong) 3.9–4.4 Å, halo II (strong) 2.4–2.6 Å, halo III (weak) 1.6–1.8 Å, and halo IV (medium) 1.3–1.4 Å. These results agree with published data on amorphous boron prepared by various methods, namely, vapor thermal decomposition on tungsten filament,<sup>4,5</sup> rapid quenching,<sup>6</sup> evaporation,<sup>7</sup> and the CVD method.<sup>8</sup> Thus the general structure of amorphous boron appears to be independent of preparation methods.

The IR absorption spectra (Fig. 1), however, show that the microstructure of the boron films depends on  $T_s$ . The spectra are characterized by one sharp and two broad bands, namely, band I at  $\sim 2560 \text{ cm}^{-1}$ , band II from 1600 to 2200  $\text{cm}^{-1}$ , and band III from 600 to 1250  $\text{cm}^{-1}$ . Band I at 2560  $\text{cm}^{-1}$  can be attributed to B—H bonds.<sup>9,10</sup> Band II is related to the three-center bonds formed by hydrogen and boron atoms and similar to those in a diborane molecule. Band II covers the four absorption bands of a diborane molecule<sup>11,12</sup> at 1602, 1755, 1915, and 2109  $\text{cm}^{-1}$ . A similar band was also observed by Tsai<sup>10</sup> in glow-discharge  $\alpha$ -B:H. Thus these two bands are related to the incorporation of hydrogen whose presence cannot be detected by x

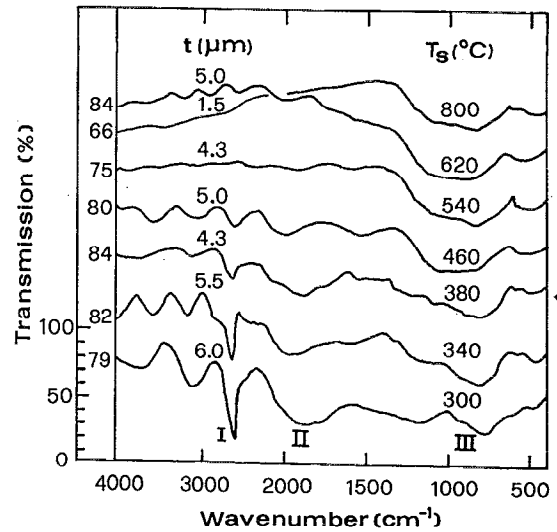


FIG. 1. IR absorption spectra of boron films deposited at different  $T_s$  ranging between 300 and 800 °C.

rays. It can be seen that absorption at bands I and II is largest at  $T_s=300 \text{ °C}$  and becomes negligible at  $T_s=540 \text{ °C}$ .

Band III exists at all  $T_s$  and, in fact, broadens with rising  $T_s$ . Thus this band must be related to the fundamental structure of  $\alpha$ -B. Crystalline boron exists in different allotropic forms based on different three-dimensional skeletons of  $B_{12}$  icosahedral units. The  $\beta$ -rhombohedral boron IR spectra<sup>13</sup> have absorption bands at 485, 550, 614, 680, 768, 848, 925, and 1235  $\text{cm}^{-1}$  while the  $\alpha$ -rhombohedral boron Raman spectra<sup>14</sup> have bands at 524, 586, 691, 774, 793, 870, 930, 1121, and 1184  $\text{cm}^{-1}$ . In comparison to band III, all the other bands are covered in boron films prepared at  $T_s=300 \text{ °C}$  except bands with wave number  $> 1000 \text{ cm}^{-1}$ . As  $T_s$  increases to 800 °C, band III broadens to include the 1235  $\text{cm}^{-1}$  band of  $\beta$ -rhombohedral boron. The presence of band III over a wide range of  $T_s$  is an indication of the presence of  $B_{12}$  icosahedral clusters in LPCVD  $\alpha$ -boron films.

The existence of  $B_{12}$  icosahedral clusters is, in fact, already inferred from x-ray diffraction patterns. This can be shown by comparing the  $d$  spacings of the halos from amorphous boron films to a suitable grouping of lattice spacings of  $\alpha$ -rhombohedral boron. The  $\alpha$ -rhombohedral lines<sup>15</sup> can be divided into five main groups as follows

- Group I: contains (01·2), (10·1), and (00·3) planes, with  $d$  ranging from 3.544 to 4.247 Å;
- Group II: contains (11·0) and (10·4) planes with  $d$  equal to 2.479 and 2.545 Å, respectively;
- Group III: contains (20·2), (02·1), (11·3), and (01·5) planes with  $d$  ranging from 2.029 to 2.180 Å;
- Group IV: contains (11·6), (21·1), (20·5), and (10·7) planes with  $d$  ranging from 1.603 to 1.666 Å; and
- Group V: contains (03·3), (30·3), (12·5), (02·7),

(00·9), (30·0), (21·4), and (01·8) planes with  $d$  ranging from 1.346 to 1.428 Å.

The first halo of  $\alpha$ -B corresponds to group I, while the strongest line from (10·1) planes in group I explains the strong intensity of this halo. Similarly, the remaining three halos are consistent with lines from the second, fourth, and fifth groups of  $\alpha$ -rhombohedral boron. The halo corresponding to the strong line of (02·1) planes in group III is not observable. The reason for this discrepancy is not known, although Otte *et al.*<sup>4</sup> and Lindquist *et al.*<sup>5</sup> both reported very weak halos with  $d$  spacings of 2.19–2.22 Å and 2.13 Å, respectively. The correspondence of the halo  $d$  spacings with  $d$  spacings from  $\beta$ -rhombohedral boron is less satisfactory. A mixture of  $\alpha$ -rhombohedral and  $\alpha$ -tetragonal boron lines does not give a better agreement either. Since the formation temperature of  $\alpha$ -rhombohedral boron (around 700–1100 °C) is lowest among all boron allotropes, it is more likely that this structure rather than  $\beta$ -rhombohedral or other forms is more favored in  $\alpha$ -B, which is usually prepared at temperatures below 800 °C. This line of thinking will be elaborated on when discussing the structure of  $\alpha$ -B $_x$ Si $_{1-x}$ .

The effect of hydrogen on the B $_{12}$  icosahedral structure in  $\alpha$ -B is also evident in band III of the IR absorption spectrum. From Fig. 1, band III for  $T_s=300$  °C shows a conspicuous dip at about 780 cm $^{-1}$ . This dip can be assigned to the B—B stretching mode across the double-hydrogen bridge as in the B $_2$ H $_6$  molecule<sup>12</sup> which has an absorption at 788 cm $^{-1}$ . The strength of the absorption at 780 cm $^{-1}$  decreases and finally disappears above  $T_s=540$  °C. This is consistent with the behavior of band I and band II, i.e., hydrogen incorporation into the solid phase becomes difficult above 500 °C.

## V. BORON-SILICON FILMS: SUBSTRATE TEMPERATURE EFFECT

The average  $d$  spacings of the x-ray diffraction halos as a function of boron content in the B $_x$ Si $_{1-x}$  films are shown in Fig. 2. Results for  $T_s=460$  and 620 °C are denoted by ● and ○, respectively. Due to the very low coating rate at 300 °C and the large thickness requirement, no x-ray data are available for this  $T_s$ . One can see that data for  $T_s$  of 460 and 620 °C fall on the same curve. Thus the structure of B $_x$ Si $_{1-x}$  films is only slightly affected by  $T_s$  and is primarily affected by film composition which will be discussed in more detail in Sec. VI.

The effect of  $T_s$  on IR absorption spectrum is very similar to the behavior in  $\alpha$ -B. Typical results for films deposited with  $R=5$  are shown in Fig. 3. As in  $\alpha$ -B, the strength of band I and band II absorption and the dip at 780 cm $^{-1}$  in band III decrease with increasing  $T_s$  and with a concomitant flattening and broadening of band III. For lower  $R$  where B content becomes smaller, band II and eventually band I may disappear even at  $T_s=460$  °C. Since all these bands are related to B—H type bonds, it is clear that the most conspicuous effect of lowering  $T_s$  is to favor the formation of B—H type bonds. It is interesting to note

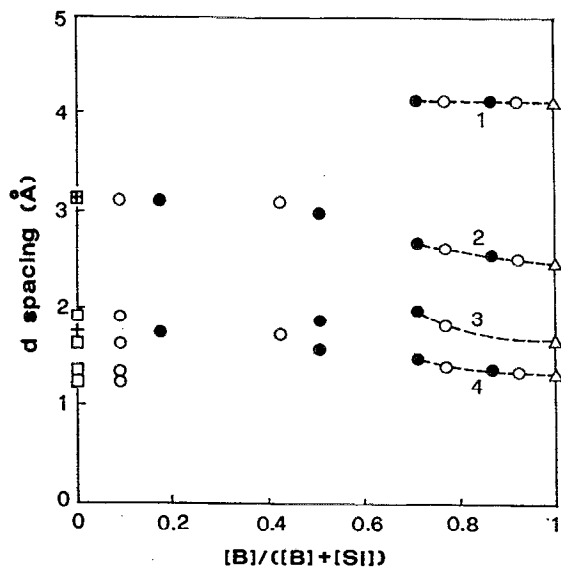


FIG. 2.  $d$  spacings of boron films and B $_x$ Si $_{1-x}$  films plotted against  $x=[B]/([B]+[Si])$ .  $\Delta$  boron films;  $\bullet$  B $_x$ Si $_{1-x}$  films deposited at 460 °C;  $\circ$  B $_x$ Si $_{1-x}$  films deposited at 620 °C;  $\square$  crystalline silicon;  $+$  amorphous silicon.

that band III exists for all  $T_s$  and for  $R$  as low as  $5 \times 10^{-3}$  and its significance will be discussed in Sec. VII.

## VI. BORON-SILICON FILMS: HIGH BORON CONTENT WITH $x > 0.6$

The x-ray diffraction patterns of this group of films are all amorphous boronlike. The dashed lines in Fig. 2 show how the  $d$  spacings from different halos vary continually with the boron content, from  $x=1$  to  $x=0.7$ . The  $d$  spacings of the first halo (curve 1) are practically independent of  $x$ , but the  $d$  spacings of the second, third, and fourth halos increase with decreasing  $x$ . The increase in  $d$  spacings is substantial, namely, from 2.5 to 2.7 Å for the second, from 1.7 to 2.0 Å for the third, and from 1.35 to 1.5 Å for the fourth halo. The third halo of boron is already very

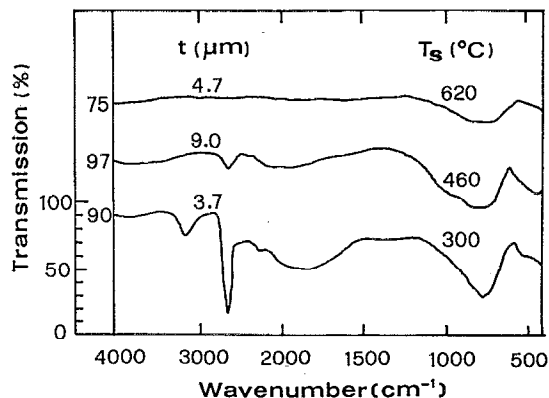


FIG. 3. Substrate temperature effect on IR absorption spectra of B $_x$ Si $_{1-x}$  films deposited with  $R=5$ .

weak and is not observable at  $x \sim 0.9$ , but it returns again at  $x \sim 0.77$ . The reason for its disappearance is not known yet.

Let us focus on the sample with  $x=0.77$ , which has a boron content close to the crystalline compound  $\text{SiB}_4$ . According to the results of Matkovich,<sup>16</sup> the characteristic lines of  $\text{SiB}_4$  can be divided into four groups.

Group I: contains (01·2) and (10·1) planes with  $d$  equal to 4.147 and 4.985 Å, respectively;

Group II: contains (01·5), (20·2), (02·1), (10·4), and (11·0) planes with  $d$  ranging from 2.308 to 3.159 Å;

Group III: contains (22·0), (12·5), (30·3), (10·7), (11·6), and (21·1) planes with  $d$  ranging from 1.582 to 2.043 Å; and

Group IV: contains (40·1), (30·6), (31·2), (22·3), (13·1), (02·7), and (01·8) planes with  $d$  ranging from 1.361 to 1.527 Å.

The  $d$  spacings of these groups roughly coincide with those deduced from the four halos of the boron-silicon films, namely, 3.8–4.6 Å, 2.35–2.94 Å, 1.70–2.00 Å, and 1.35–1.50 Å. The strong lines from (10·4) and (02·1) of  $\text{SiB}_4$  is accompanied by the second halo with the strongest intensity. Thus there is a direct correlation between the structure of  $\text{SiB}_4$  and the  $a\text{-B}_{0.77}\text{Si}_{0.23}$  film. The structure of  $\text{SiB}_4$  is close to  $\alpha$ -rhombohedral boron and can be understood from the structure of  $\text{B}_{12}\text{C}_3$ , in which a three-atom carbon chain (C—C—C) is inserted into the cavity of each  $\alpha$ -rhombohedral boron unit cell. To form  $\text{SiB}_4$  from  $\text{B}_{12}\text{C}_3$ , two silicon atoms replace two carbon atoms of the C—C—C chain, while the remaining silicon atoms statistically replace boron atoms in the icosahedron.<sup>17</sup> Comparing with the lattice parameters of  $\alpha$ -rhombohedral boron, the hexagonal lattice parameter  $a$  (6.35 Å) of  $\text{SiB}_4$  increases by about 30% but  $c$  (12.69 Å) only increases by about 1%. Thus the formation of  $\text{SiB}_4$  can be envisaged as adding silicon atoms into  $\alpha$ -rhombohedral boron with the result of “laterally” expanding the rhombohedral unit cell. The same line of thought may be applied to explain the variation of  $d$  with  $x$  in  $a\text{-B}_x\text{Si}_{1-x}$  films for  $x > 0.7$ . One may start from  $a\text{-B}$  with a structure close to the  $\alpha$ -rhombohedral structure. By inserting more and more silicon atoms interstitially into the cavities of the irregular rhombohedra formed by  $\text{B}_{12}$  icosahedral clusters in  $a\text{-B}$ , the structure gradually approaches that of crystalline  $\text{SiB}_4$ . The size of the rhombohedral cells eventually increases as a result of increasing silicon content, consistent with experimental observation.

The IR absorption spectra of this group are shown in Fig. 4 and review another aspect, the microstructure. In general, the effect of decreasing boron content (decreasing  $R$ ) has a similar effect as increasing  $T_s$ , i.e., the strength of absorption bands related to B—H type bonds, namely, bands I, II, and the dip at  $780\text{ cm}^{-1}$ , all decreases with  $R$ . One might expect then new absorption bands relating to Si—H type bonds (at  $2000\text{--}2100$ ,  $890$ ,  $840$ , and  $650\text{ cm}^{-1}$ ) would appear as reported by Tsai<sup>10</sup> on silicon-boron films

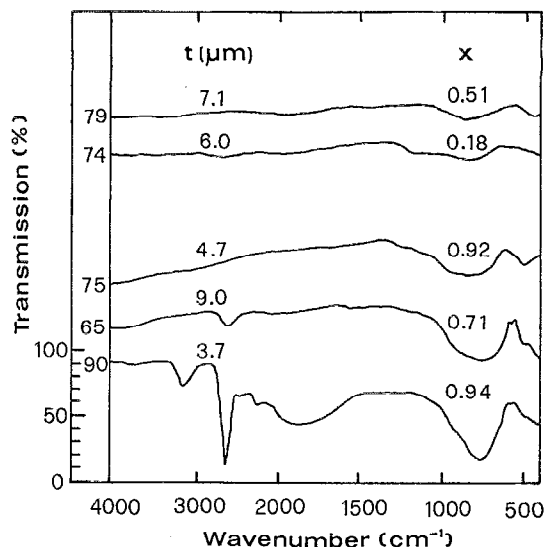


FIG. 4. IR absorption spectra of  $\text{B}_x\text{Si}_{1-x}$  films with  $x=0.92$  ( $T_s=620^\circ\text{C}$ );  $x=0.71$  ( $T_s=460^\circ\text{C}$ );  $x=0.94$  ( $T_s=300^\circ\text{C}$ );  $x=0.51$  ( $T_s=460^\circ\text{C}$ ); and  $x=0.18$  ( $T_s=460^\circ\text{C}$ ).

prepared by the glow discharge method. However no such absorption bands can be found in our LPCVD  $a\text{-B}_x\text{Si}_{1-x}$  films. This result strongly suggests that silicon atoms prefer to bond with boron atoms rather than with hydrogen atoms in the LPCVD processes and leading to the low hydrogen content in  $a\text{-B}_x\text{Si}_{1-x}$  films. Evidently the deposition mechanism between the LPCVD and the glow discharge method is different. In the LPCVD method, the decomposition of silane and diborane is solely a thermal process, while in the glow discharge method, the chemistry is primarily determined by the energetic collisions between neutral and charged radicals with hydrogen remaining intact with silicon and boron. An indirect support of our observation is given by Murase,<sup>18</sup> who found that the incorporation probability of a Si atom is about 3 times higher at the B site than at the Si site in a LPCVD process.

## VII. BORON-SILICON FILMS: LOW BORON CONTENT WITH $x < 0.6$

The change of structure from high boron content to low boron content films can be best traced (in Fig. 2) in the direction of decreasing  $x$ . The high boron-content films have amorphous boronlike diffraction patterns with four characteristic halos. As  $x$  decreases to 0.51, only three halos can be observed. The first halo has a  $d$  spacing of about 3 Å, which is close to the  $d$  spacing for amorphous silicon and corresponds to the (111) plane of crystalline silicon ( $d=3.1317$  Å). The second halo has a  $d$  spacing of about 1.9 Å, which is smaller than the  $d$  spacing of the third halo of  $a\text{-B}$ , while the  $d$  spacing of the third halo ( $\sim 1.6$  Å) is larger than the  $d$  spacing of the fourth halo of  $a\text{-B}$ . The last two halos tend to merge together as  $x$  decreases. This merging becomes complete at  $x=0.43$  and forms a halo with  $d$  spacing of about 1.6–1.9 Å that corresponds to a mixture of (220) and (311) planes of crystalline silicon.

Thus, from the structural point of view, films with such a high value of  $x=0.43$  can still be called amorphous silicon. This is a little surprising since the boron content is much higher than the solid phase solubility of boron in crystalline silicon that is only 0.81 at. % at 25 °C. This result, however, is consistent to a previous report on transport properties of  $a$ -Si:B (Ref. 1) that shows that  $a$ -Si:B with  $x=0.4$  still behaves like heavily doped  $a$ -Si. At  $x=0.09$  ( $T_s=620$  °C), the film becomes polycrystalline, with all the characteristic lines of crystalline silicon. The boron content of this sample still exceeds the solid solubility of boron in crystalline silicon. One may speculate that in these films the majority of boron atoms segregate at the grain boundaries. It should be noted that at this composition films are only amorphous when prepared at  $T_s < 560$  °C.<sup>19</sup>

As pointed out in Sec. VI, decreasing the boron content of the film is similar to raising  $T_s$ . Hence no absorption bands corresponding to B—H and Si—H type bonds appear. The spectra for films deposited at  $T_s=460$  °C are simple, with weak absorption corresponding to band III of the high boron content films (Fig. 4). For the sample with  $x=0.18$ , x-ray pattern shows that it has an  $a$ -Si structure. However a noticeable band III in the IR spectra still exists. Since band III is related to icosahedral boron clusters, its presence means that formation of such clusters is still possible in this low concentration of boron. However their size is probably small enough to evade detection by our x-ray experiments.

Through the deconvolution of optical absorption spectra of the boron-silicon films, the strong optical absorption at the near-infrared region was explained by the existence of a localized impurity electron band situated above  $E_v$ .<sup>20</sup> Electrical conductivity and thermoelectric power measurements on low boron content films<sup>1</sup> also showed that an impurity band exists at about 0.2 eV above  $E_v$ , which limits the position of Fermi level relative to  $E_v$  to not less than about 0.25 eV by boron doping to  $a$ -Si. These observations indicate that the impurity band can easily be formed in LPCVD prepared films and is probably related to the icosahedral clusters formed in the  $a$ -Si network according to the present investigation (see Sec. VI). Consequently, the existence of this impurity band can pin the Fermi level<sup>1</sup> and lower the doping efficiency of boron atoms in the  $a$ -Si network. Therefore, although LPCVD  $a$ -Si films have a smaller band tail than glow discharge  $a$ -Si:H films, the doping efficiency of boron in LPCVD  $a$ -Si films can only be further improved if some way can be found to suppress the easy formation of icosahedral clusters during LPCVD film deposition.

### VIII. SI INCORPORATION EFFICIENCY: LPCVD VS GLOW DISCHARGE

In Sec. VI, we pointed out that the deposition mechanism in the LPCVD process is different from that of the glow discharge deposition process. This difference is more evident when one compares the silicon incorporation efficiency  $\eta$  in the films prepared by these two methods.  $\eta$  is defined as

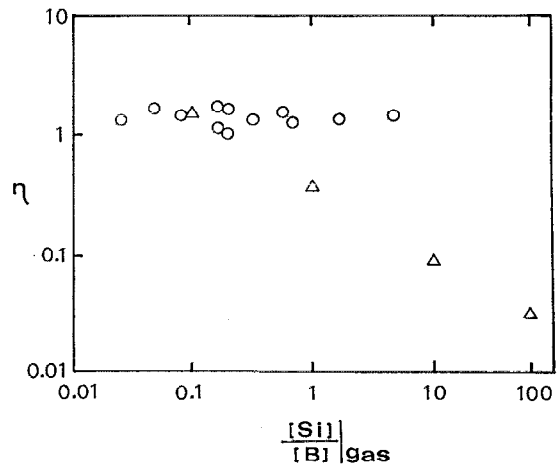


FIG. 5. Silicon incorporation efficiency  $\eta = ([\text{Si}]/[\text{B}]_{\text{film}})/([\text{Si}]/[\text{B}]_{\text{gas}})$  in  $\text{B}_x\text{Si}_{1-x}$  films plotted against  $[\text{Si}]/[\text{B}]_{\text{gas}}$ ;  $\Delta$ : samples prepared by the LPCVD method;  $\circ$ : samples prepared by the glow discharge method.

$$\eta = \frac{(N_{\text{Si}}/N_{\text{B}})_{\text{solid}}}{(N_{\text{Si}}/N_{\text{B}})_{\text{gas}}},$$

where  $N_{\text{Si}}$  and  $N_{\text{B}}$  are the numbers of silicon atoms and boron atoms, respectively. The subscript <sub>solid</sub> means that the number is counted in solid film, while <sub>gas</sub> refers to that gas in the gas mixture inside the reactor during deposition. Figure 5 shows  $\eta$  plots as a function of  $(N_{\text{Si}}/N_{\text{B}})_{\text{gas}}$  for two cases.  $\Delta$  denotes data for LPCVD films deposited at 460 °C and  $\circ$  denotes data for glow discharge films deposited at 270 °C. For the LPCVD case,  $\eta$  depends strongly on  $(N_{\text{Si}}/N_{\text{B}})_{\text{gas}}$ . For example, at  $(N_{\text{Si}}/N_{\text{B}})_{\text{gas}}=100$ ,  $\eta$  is 0.032, which means that most of the silicon atoms in the gas phase cannot go into the solid film.  $\eta$ , however, increases dramatically with decreasing  $(N_{\text{Si}}/N_{\text{B}})_{\text{gas}}$  and reaches 1.5 for  $(N_{\text{Si}}/N_{\text{B}})_{\text{gas}}=0.1$ . This means that the decomposition of silane is greatly enhanced if a large proportion of diborane is present in the gas mixture, resulting in a high Si incorporation efficiency in the solid film. On the contrary,  $\eta$  is practically independent of  $(N_{\text{Si}}/N_{\text{B}})_{\text{gas}}$  for the glow discharge process and remains around 1.5. Here, the energetic ions within the plasma provide enough energy to break up the silane molecules such that the fraction of silicon incorporated into the solid film roughly equals the fraction of silicon in the gas mixture.

### IX. CONCLUSIONS

The present investigation shows that x-ray diffraction patterns and IR absorption spectra can give complementary information about the structural change when an increasing number of silicon atoms is incorporated into the amorphous boron matrix. From x-ray results, we observe a gradual transition from the amorphous boron structure that is closely related to crystalline  $\alpha$ -rhombohedral boron through the  $\text{SiB}_4$  structure to the amorphous silicon structure. The transition to an  $a$ -Si structure is complete at a

surprisingly high boron concentration, namely, around 40 at. %. Thus amorphous silicon films containing such a high boron concentration can still be called boron-doped amorphous silicon. This is consistent with the reported transport results on such films.<sup>1</sup> Infrared absorption spectra reveal that the effect of silicon incorporation on the structural change is more subtle than that observed from x-ray diffraction. As expected, low substrate temperatures, particularly at 300 °C, favor the formation of B—H bonds that becomes unfavorable at  $T_s$ , above 540 °C. However, it is surprising to find that the presence of boron suppresses the formation of Si—H bonds in high silicon-content films. This behavior is in sharp contrast to films prepared by the glow discharge method, where strong Si—H absorption is observed. Thus, in the thermal LPCVD process, boron atoms tend to cluster around silicon atoms eliminating the formation of Si—H bonds. Another interesting feature of the IR absorption spectra is the predominance of an absorption band related to the presence of boronlike icosahedral clusters in all films with boron concentration as low as 17.6 at. %. This again supports the idea that boron tends to cluster around silicon. In fact, a dominant impurity band lying about 0.2 eV above the valence mobility edge has been observed in boron doped LPCVD *a*-Si films. We suggest that the impurity band is related to the boronlike icosahedral clusters found in this investigation.

## ACKNOWLEDGMENT

This work was partly supported by the Hong Kong Research Grants Council.

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