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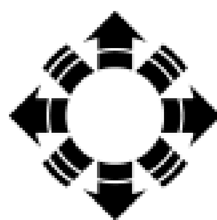

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ABSTRACT

BGaInAs can potentially be used in strain-free high-efficiency III-V solar cells, but the growth of sufficiently high-quality epitaxial BGaInAs using diborane has proven difficult. We compare the use of alternative boron precursors (trimethylboron [TMB], triethylboron [TEB], and boron trifluoride [BF_3]) with diborane for the MOCVD growth of these boron-containing III-V alloys. We find that TMB and BF_3 do not result in significant boron incorporation into GaAs. TEB does result in boron incorporation in a manner very similar to diborane. Both diborane and TEB incorporate more efficiently using triethylgallium (TEG) rather than trimethylgallium (TMG), making TEG a preferred source of gallium for BGaAs epitaxy. Using TEB together with TEG, a higher boron composition (x = 4% – 7%) has been achieved than has been previously reported, but we are still unable to achieve high- quality BGaInAs with the correct composition for solar cell applications.

1. Introduction

$B_xGa_{1-x-y}In_yAs$ lattice-matched to GaAs has been shown to be an interesting material for solar cell applications [1,2]. We have demonstrated zinc-blende alloys of $B_xGa_{1-x}As$ with boron concentrations (x) as high as several percent grown epitaxially on GaAs by metal-organic chemical-vapor deposition (MOCVD) using diborane (B_2H_6) [1] It would be beneficial, though, to significantly increase the boron concentration in a high quality alloy material. The use of diborane for MOCVD growth of $B_xGa_{1-x}As$ and $B_xGa_{1-x-y}In_yAs$ has proven to be less than ideal due to parasitic gas-phase reactions, highly temperature-dependent boron incorporation, non-linear boron incorporation, and limited boron incorporation before the onset of structural breakdown [3]. In this paper, we compare the use of various precursors for MOCVD growth of BGaAs [4].

2. Diborane

Using a 3% diborane (B_2H_6) in hydrogen mixture, we have achieved boron compositions of up to about x =3% – 5% in zinc-blende $B_xGa_{1-x}As$. An apparent miscibility gap seems to drive the degradation of the crystal structure and stoichiometry of $B_xGa_{1-x}As$ beyond this point. Figure 1 shows the boron incorporation as a function of growth temperature (circles show diborane data). Both the incorporation efficiency and maximum achievable concentrations before degradation drop off at temperatures greater than 600°C. Using TMG, the incorporation also drops off below 550°C; but using TEG, the incorporation remains constant to 500°C. Figure 2 shows the incorporation behavior as a function of the B fraction of the group III sources grown at temperatures that provide maximum incorporation. An important difference between the growth of BGaAs using diborane with TMG and TEG has been observed. The solid incorporation of boron increases quadratically with the boron fraction of the group III source in the vapor phase when TMG is used, but linearly (and with greater efficiency) when TEG is used. A reduction of the growth rate has been shown [3] to be correlated to a function of the input gas-phase mole fraction of the sources, $[B_2H_6][AsH_3]^{1/3}[TMG]^{-1/2}$, independent of growth temperature over the range of 600° – 700°C.

3. Trimethylboron (TMB)

TMB is a readily available boron source that has been used as a doping source in silicon and diamond growth. We used a 15% TMB in hydrogen mixture. The square data points in Figure 1 show the incorporation of boron using TMB with TMG and arsine over a range of temperatures. Very low boron incorporation ($<5x10^{18}$ cm^{-3}) was observed even when the ratio of TMB to TMG was varied from one to 1000.

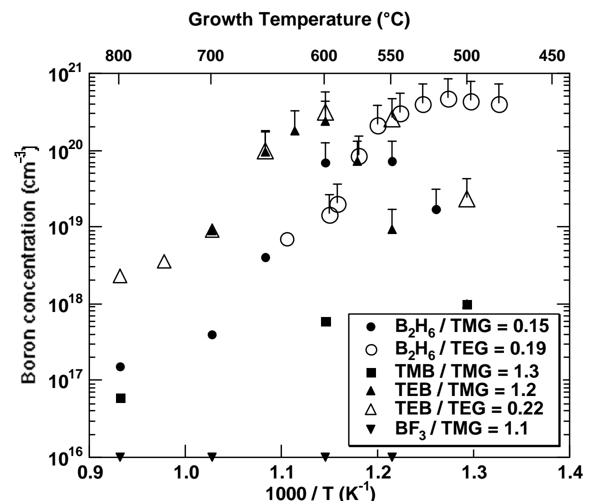

Fig. 1. Boron composition in $B_xGa_{1-x}As$ as a function of growth temperature using a variety of boron and gallium sources. Boron concentrations were determined from X-ray (with error bars) and SIMS (no error bars). Each source combination was taken under constant conditions varying only the temperature, but these conditions vary between source combinations. The molar ratio of boron source to gallium source is listed in the legend.

4. Triethylboron (TEB)

We have bubbled H_2 through a liquid TEB source with both TMG and TEG to grow $B_xGa_{1-x}As$. The incorporation of boron as a function of temperature is shown as triangle data points in Figure 1. The incorporation falls off dramatically at temperatures greater than 600°C for both TMG (filled points) and TEG (empty points), similar to diborane. Using TMG, the incorporation also drops off immediately below 600°C; but using TEG, the incorporation remains constant to about 550°C.

Figure 2 compares the TEB data at 600°C with diborane. Surprisingly similar to diborane, the incorporation follows a quadratic dependence when using TMG, but a linear dependence when using TEG. Similar compositions of boron in $B_xGa_{1-x}As$ (x=3% – 5%) have been achieved using TEB and TMG as with diborane. Using TEB and TEG with a high arsine/TMG ratio of 263, though, at least 40% more B was incorporated into specular $B_xGa_{1-x}As$ than has previously been demonstrated using diborane. But again, attempts to increase the boron compositions beyond this point result in structural and stoichiometric breakdown. The quality (as determined by quantum efficiency measurements of cells) of the material grown with TEB and TEG, though, was not significantly different from that grown with diborane.

Another similarity between the use of diborane and TEB was observed when high arsine and TEB flow rates were used together. Although no reduction in the growth rate was observed using lower arsine flow rates (V/Ga ratio of 26), the actual growth rate of $B_xGa_{1-x}As$ using higher arsine flows (V/Ga ratio of 263) was significantly reduced compared to growth without TEB [4]. This growth rate reduction was observed using both TEG and TMG. These results do not quantitatively follow the trends of the growth rate reduction using diborane, TMG, and arsine. In particular, the reduction in growth rate using TEB, TEG, and arsine increases as a function of temperature over the range of 550° – 650°C. Nevertheless, these data may indicate that arsine and TEB react together with TMG or TEG in the gas-phase, depleting the Ga source before reaching the substrate.

The similarities between diborane and TEB suggest that a common intermediate species (e.g., BH_x radicals) may be formed in the gas phase by both sources.

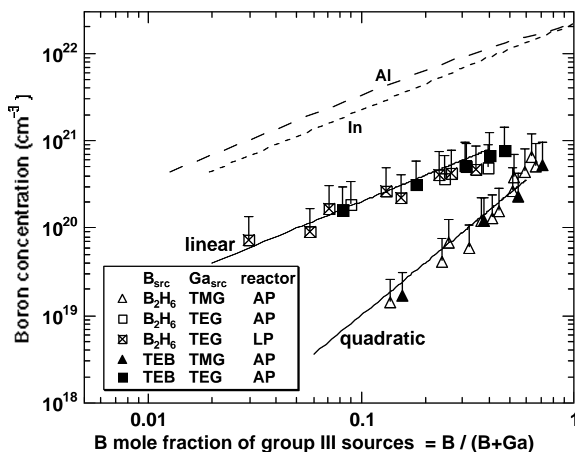

Fig. 2. Boron composition in $B_xGa_{1-x}As$ as a function of the boron mole fraction of the group III gas sources. (Note: diborane contributes 2 moles B per molecule.) All data were taken at a growth temperature of 600°C, except the data taken in the low-pressure (LP) reactor, which was taken at 512°C. Nominal growth rates were 2 – 5 µm/h and V/III ratios were 26 – 300. The composition was determined from X-ray data. Solid lines show linear and quadratic dependencies. Dashed lines show typical Al and In incorporation behavior using TMA and TMI, respectively

5. Boron trifluoride (BF_3)

We also tried using a 10% BF_3 in helium mixture for growth of $B_xGa_{1-x}As$. Figure 1 shows no incorporation of boron (less than or equal to the SIMS background of $1x10^{16}$ cm^{-3}) using BF_3 over the temperature range of interest for MOCVD growth. Thermodynamic calculations indicate that BF_3 remains extremely stable to well over 700°C. Because growth of BGaAs appears to require low temperatures, BF_3 does not seem to be an appropriate boron source.

6. Summary

We have studied several boron precursors for $B_xGa_{1-x}As$ growth by MOCVD. Neither BF_3 nor TMB result in significant incorporation, but diborane and TEB can be used to achieve boron compositions (x) up to several percent. TEG has been shown to be a more favorable Ga source than TMG in the growth of $B_xGa_{1-x}As$ because of the higher incorporation efficiency of boron. Using TEB together with TEG, a higher boron composition (x = 4% – 7%) has been achieved than has been previously reported using diborane, but problems of parasitic gas-phase reactions and limited maximum boron concentrations still exist with all of the sources studied here.

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