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Article Title: Elemental boron doping behavior in silicon molecular beam epitaxy

Year of publication: 1991

Link to published version: [http://dx.doi.org/ 10.1063/1.104614](http://dx.doi.org/10.1063/1.104614)

Publisher statement: none

Elemental boron doping behavior in silicon molecular beam epitaxy

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(Received 5 July 1990; accepted for publication 2 October 1990)

Boron-doped Si epilayers were grown by molecular beam epitaxy (MBE) using an elemental boron source, at levels up to $2 \times 10^{20} \text{ cm}^{-3}$, to elucidate profile control and electrical activation over the growth temperature range 450–900 °C. Precipitation and surface segregation effects were observed at doping levels of $2 \times 10^{20} \text{ cm}^{-3}$ for growth temperatures above 600 °C. At growth temperatures below 600 °C, excellent profile control was achieved with complete electrical activation at concentrations of $2 \times 10^{20} \text{ cm}^{-3}$, corresponding to the optimal MBE growth conditions for a range of $\text{Si}/\text{Si}_x\text{Ge}_{1-x}$ heterostructures.

Boron has become the preferred *p*-type dopant in silicon molecular beam epitaxy (Si-MBE), most authors preferring to use a compound-boron source.^{1–5} Recent interest in silicon germanium structures requires an improved understanding of boron doping kinetics particularly at low substrate temperature ($< 550 \text{ °C}$) and for device applications at high doping levels ($> 10^{19} \text{ cm}^{-3}$).² For example, Jackman *et al.*³ have reported redistribution of boron at levels above the solubility limit in MBE-grown layers, which has important consequences for the growth of device structures. This and similar previous studies,^{4,5} have been encumbered by the presence of oxygen from compound-boron doping sources, which has led to incorporation of oxygen, impairing crystalline quality. In this letter we report on the influence of growth temperature on the incorporation behavior of boron using an elemental boron source.

For this study epilayers containing boron-doped regions 50 nm thick, separated by 200 nm of undoped material, were grown on Si (100) substrates at temperatures from 900 to 450 °C. The boron layers were doped at $2 \times 10^{20} \text{ cm}^{-3}$ in structure A—well above reported bulk solid solubility limits,⁶ and at $6 \times 10^{18} \text{ cm}^{-3}$ in structure B.

The secondary-ion mass spectrometry (SIMS) profile of structure B is given in Fig. 1. Excellent profile control was achieved over the entire range of substrate temperatures employed. There is no evidence of precipitation effects or profile smearing by segregation, although solid-state diffusion produces discernible broadening of the profile grown at temperatures above 800 °C. Electrochemical capacitance-voltage (*e-C-V*) measurements are in excellent agreement with the SIMS results, indicative of complete activation at all temperatures.

SIMS and *e-C-V* profiles for structure A are presented in Figs. 2 and 3, respectively. Major perturbations in these profiles are evident between deposition temperatures of 700 and 900 °C manifested by (a) a $\sim 15 \text{ nm}$ -wide spike with higher than intended concentration and (b) a shoulder extending into the nominally undoped region. Evidence

from *e-C-V* (Fig. 3) and spreading resistance profile measurements suggests that the shoulders are fully activated but the spikes are not—the shoulders in fact define the electrically activated incorporation limit at these substrate temperatures.⁶

For the boron-doped regions in structure A grown at 750 and 800 °C, two chemical spikes are seen close to the interfaces between doped and undoped silicon. Figure 4 shows a bright field cross-sectional transmission electron microscopy (TEM) image of these features taken in a micro beam symmetrical [110] condition. The highly doped ($2 \times 10^{20} \text{ cm}^{-3}$) layers appear as uniform dark bands, only for the lower growth temperatures where the boron is completely incorporated. Above 650 °C precipitation occurs, the amount of active boron incorporation falls as boron goes into the formation of precipitates, with excess boron accumulating at the surface of the growing layer. This is seen in the SIMS profile by the shoulders between 1 and $5 \times 10^{19} \text{ cm}^{-3}$, and in the TEM image by the absence of

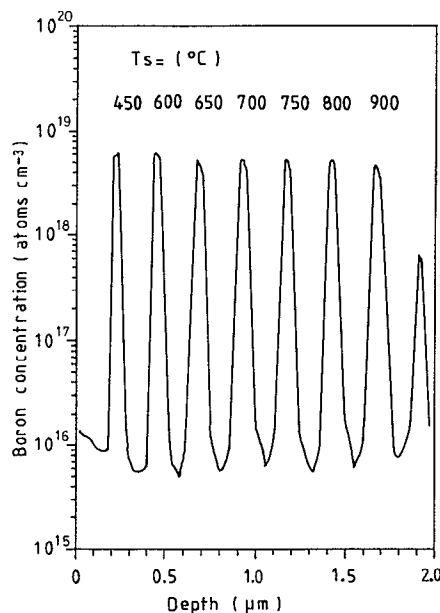


FIG. 1. SIMS depth profile (total boron) of structure B using 4 keV O_2^+ primary ions. Boron-doped regions were grown at different substrate temperature (T_s , °C) with a peak doping level of $6 \times 10^{18} \text{ cm}^{-3}$.

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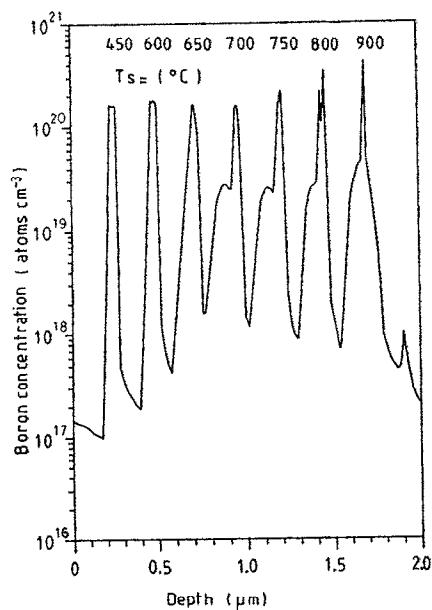


FIG. 2. SIMS depth profile (total boron) of structure A obtained using 4 keV O_2^+ primary ions. Boron-doped regions were grown at different substrate temperature (T_s , °C) with a peak doping level of $2 \times 10^{20} \text{ cm}^{-3}$.

appreciable contrast other than from the precipitates. At 750 °C individual precipitates can be resolved, at 800 °C they are confined to two bands at the top and bottom of the boron doped region, and at 900 °C they are confined to a single layer where each precipitate is approximately 10 nm in diameter. Boron precipitation is driven by the doping concentration gradient, where the strain field is a maximum, thus producing two quasi-planar distributions at the leading and trailing edges of the doped region. However the final distribution of precipitates will also be affected by diffusion effects.

This work indicates that precipitation processes which distort profiles at the higher growth temperatures are ki-

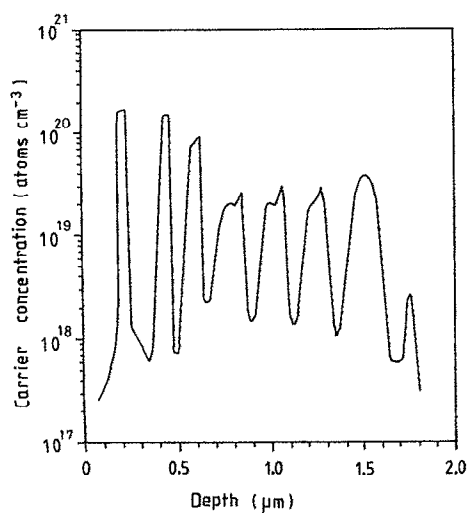


FIG. 3. Electrochemical capacitance-voltage profile of sample with a peak doping level of $2 \times 10^{20} \text{ cm}^{-3}$ (structure A).

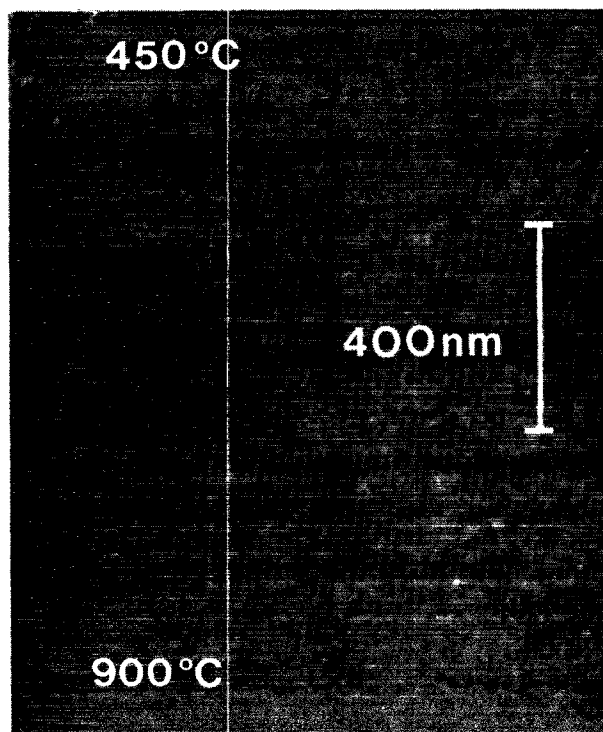


FIG. 4. XTEM micrograph of sample with a peak doping level of $2 \times 10^{20} \text{ cm}^{-3}$ (structure A). Boron-doped regions appear as contrasting bands, precipitates as narrow dark lines, approximately 10 nm in width.

netically limited at substrate temperatures below 600 °C and substitutional site occupancy is preferred at these lower temperatures.

The shoulders seen in the SIMS profile of structure B in Fig. 2 provide evidence of surface segregation occurring during growth but only when the solid solubility limits are exceeded, leading to the release of boron at the surface of the growing epilayer. Solid-state diffusion towards the substrate is evident at the highest growth temperature used (right-hand side of the spike formed at 900 °C in Fig. 2), but surface segregation accounts for the major dopant redistribution seen at these substrate temperatures, the width of the shoulders being far in excess of solid-state diffusion lengths at these temperatures.⁶ The shoulders are formed in the growth direction only, since the growing surface is the primary site for segregation. The segregation processes leading to the formation of the shoulders are temperature dependent since the distribution of dopant in the shoulders varies with growth temperature.

For growth below 600 °C boron precipitation and segregation are inhibited and excellent profile integrity is observed. For the boron-doped region grown at 450 °C in Fig. 2 the leading edge profile abruptness is better than 2 nm/dec (the resolution of the SIMS technique) and comparison with the carrier concentration profile in Fig. 3 suggests complete dopant activation.

In conclusion, boron-doped layers were grown over a range of substrate temperatures to investigate their dependence on incorporation behavior using an elemental

source. At growth temperatures below 600 °C, 100% activation at all doping levels investigated (up to $2 \times 10^{20} \text{ cm}^{-3}$) and a profile abruptness of 2 nm/dec was accomplished. At growth temperatures above 650 °C and doping levels above $\sim 1 \times 10^{19} \text{ cm}^{-3}$, severe profile distortion occurred, due to precipitation and subsequent surface accumulation of boron, giving rise to the formation of shoulders in the growth direction.

At the low growth temperatures needed for Si/Si_xGe_{1-x} structures (< 550 °C), elemental boron doping has the advantage over the use of compound sources in the elimination of severe oxygen incorporation.

In a follow-up paper we address the stability of highly doped material grown at low temperature with respect to

ex situ anneals and discuss results of solid solubility of boron in Si-MBE.

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