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Boron Doping in Silicon Molecular Beam Epitaxial Film by Coevaporation of Boron Oxide

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Boron doping with a high carrier concentration and steep doping profile has been realized in Si MBE using a usual pyrolitic boron nitride Knudsen cell with a boron oxide source. Carrier concentration was independent of substrate temperature and proportional to the inverse of the growth rate and reached as high as 7×10^{19} cm^{-3}.

1. Introduction

Epitaxial silicon films prepared by molecular beam epitaxy (MBE) are of particular interest where a well-controlled sharp doping profile is required. Using usual Knudsen cell (K-cell), metallic gallium (Ga) and antimony (Sb) are preferably used as a doping source material.[1] Among the acceptor impurities, boron is the most widely used in silicon device technology. The use of Ga is limited due to its high diffusivity in SiO_2 masking film. But, boron is not easy to be evaporated from usual K-cell with pyrolytic boron nitride (PBN) crucible, because of its high evaporation temperature (1300 - 2000 °C). Kubiak et al.[2] tried to use boron itself as a source in a special high temperature K-cell. However, the high heating temperature may make various kinds of impurities desorb from the cell materials. Such problems are overcome by using low-energy ion implantation during Si MBE,[3] however ion implantation technique brings other problems, expensive equipment cost and vacuum degradation.

In this paper, we report a study of boron doping during Si MBE by evaporation of B_2O_3 from a usual PBN K-cell.

2. Experimentals

The MBE system (ANELVA Model MBE-430) consists of three chambers (deposition, analysis and cassette entry lock). Deposition chamber is cryo-pumped to a base pressure of 1×10^{-10} Torr. Si source was a high purity 3000 Ohm-cm FZ crystal silicon rod which was evaporated by an E-gun (6 KW). A 4-inch substrate was heated by a graphite heater with temperature uniformity within ±10 °C.

Before MBE growth, (100) substrates were cleaned by particular surface cleaning process developed by us; the ozone bubbling and silicon predeposition method.[4] Si MBE films of thickness 0.2 - 1.5 µm were deposited at 1 - 20 Å/sec growth rate and 650 - 800 °C growth temperature. Sintered plates of boron nitride (BN) combined with B_2O_3 were evaporated from a usual PBN K-cell. The electrical properties of grown films were measured by the four-probe sheet resistance method and Hall measurement. Secondary ion mass spectroscopy (SIMS) was used to determine the dopant and its profile. Surface defect density in the film was determined by etch pits after Wright etching.

3. Results

Carrier concentration (C_B) dependence on cell temperature (T_{cell}) is shown in Fig. 1. C_B variation was fitted with a function of $C_B = C_0 \cdot \exp(-5.4(eV)/kT)$ at $T_{cell} > 1100$ °C.

C_B dependence on substrate temperature (T_{sub}) is shown in Fig. 2. C_B was constant in this T_{sub} range from 650 - 800 °C, therefore, the sticking

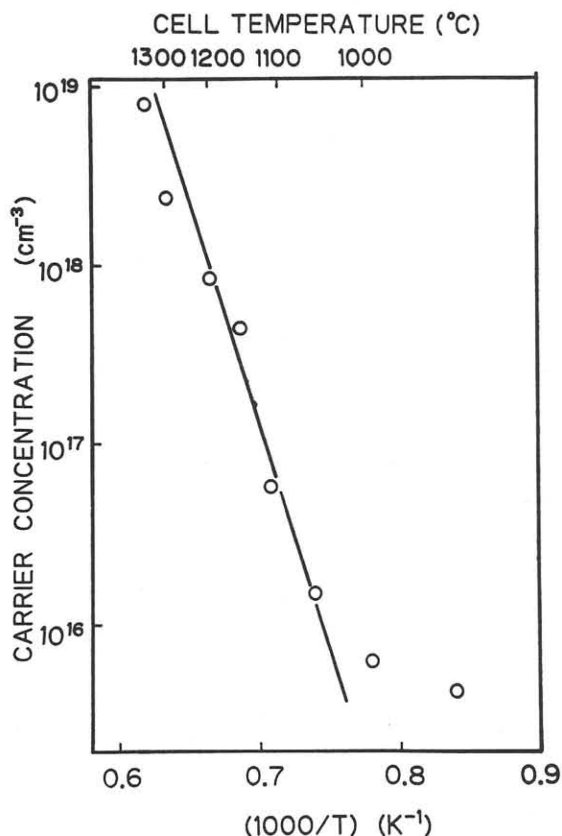

Fig. 1. Carrier concentration (C_B) dependence on B_2O_3 cell temperature (T_{cell}).

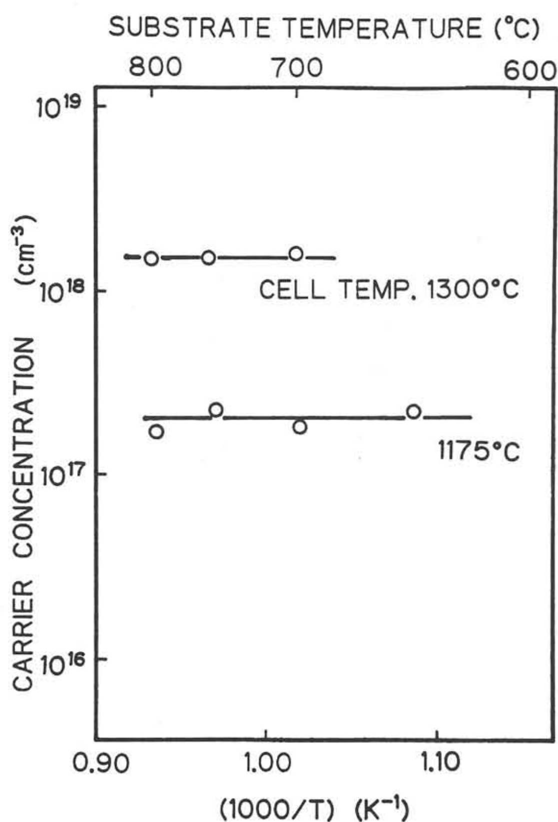

Fig. 2. Carrier concentration (C_B) dependence on substrate temperature (T_{sub}).

coefficient of boron seems to be independent of growth temperature. C_B dependence on growth rate (R_{gr}) is shown in Fig. 3, where C_B was proportional to the inverse of R_{gr}. From these results in Fig. 2 and 3, the sticking coefficient of boron is found to be unity.

To check the impurity profile controllability, K-cell shutter was programed to be open and closed during the film growth. The SIMS result of this film is shown in Fig. 4. The profile steepness was very well and the transition layer thickness was as thin as 300 Å.

Hall mobility (μ_H) were plotted as a function of carrier concentration in Fig. 5. These data were well fitted with Irvin curve except in the doping range over 10^{19} cm^{-3}.

To determine the activation efficiency, heat treatments were carried out with 0.2 µm thick B doped films. Annealing condition is 700, 800, 900 or 1000 °C in N_2 for 1 hour. The Hall measurement results are listed in Table 1. When annealing temperature was 900 °C or below, C_B was not changed, but after 1000 °C annealing, C_B was

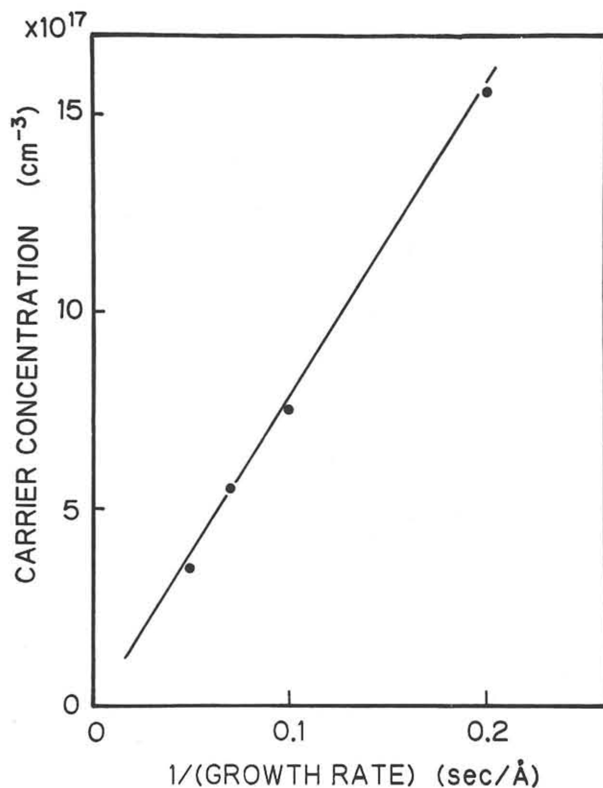

Fig. 3. Carrier concentration (C_B) dependence on growth rate (R_{gr}).

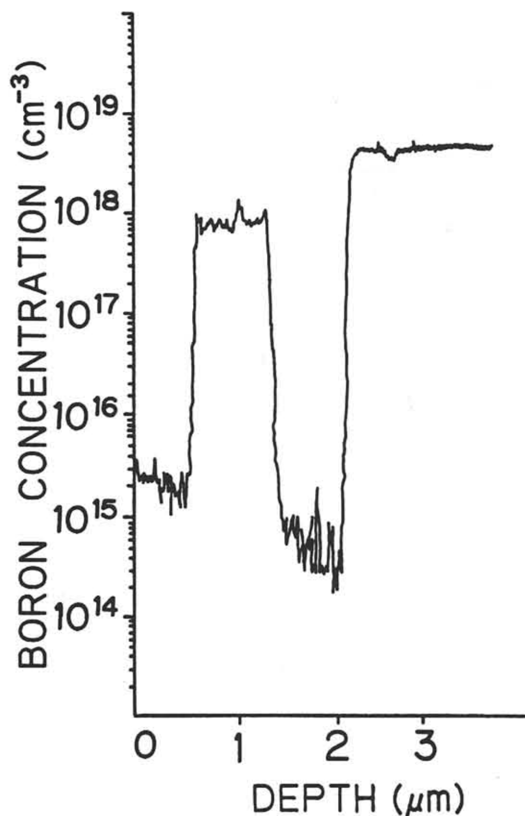

Fig. 4. SIMS profiling of an MBE film obtained by sequent K-cell shutter opening and closing.

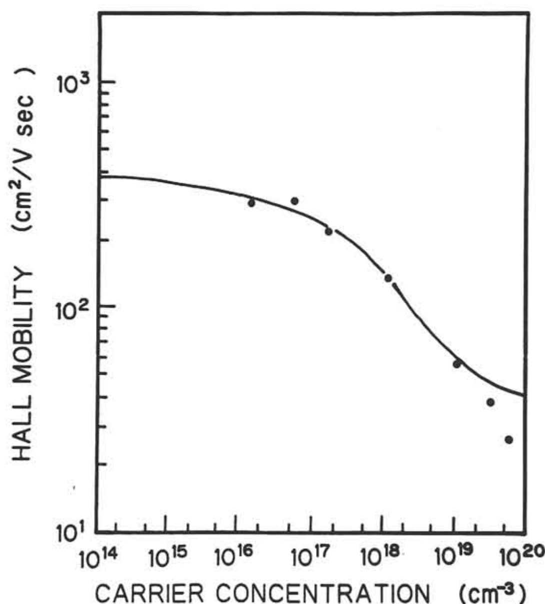

Fig. 5. Hall mobility (μ_H) dependence on carrier concentration (C_B). Solid line is the theoretical relation (Irvin curve).

Table 1. Carrier concentration (C_B) and Hall mobility (μ_H) of as-grown film and after annealing. (n-type 1000 Ohm-cm FZ (100) substrate, 1300 °C cell temperature, 700 °C substrate temperature, 0.2 um epitaxial thickness, and 1 hour annealing time.)

ANNEALING TEMPERATURE	as grown	700°C	800°C	900°C	1000°C
CARRIER CONCENTRATION (cm^{-3})	1.28×10^{18}	1.28×10^{18}	1.28×10^{18}	1.30×10^{18}	1.39×10^{18}
HALL MOBILITY (cm^2/V sec)	118	119	119	121	120

somewhat increased. If B atoms doped in MBE film were assumed to be fully activated after 1000 °C annealing, as grown activation coefficient of B atoms is calculated as 92 %. Hall mobility values as grown and after anneal were almost equal to 120 cm^2/V·sec.

Finally, lattice defect density in MBE films was nearly equal to the density in non-doped films as low as 10^2 cm^{-2} level except for heavily doped films with carrier concentration more than 10^{19} cm^{-3}, where etch pits were counted as many as 10^7 cm^{-2}.

4. Discussion

As shown in Fig. 1, an activation energy for boron evaporation process was calculated to be 5.4 eV, which is nearly equal to the activation energy of 5.6 - 5.9 eV for simple boron vapor pressure[5].

This agreement seems to indicate that boron is evaporated as a simple boron atom after reduction of B_2O_3. However, according to the quadrupole mass spectroscopy of flux from B_2O_3 source, signal increases at the mass number corresponding to BO and B_2O molecules were also detected from the heated B_2O_3 source as well as the increase at the mass number of B. Vapor from the B_2O_3 source seems to contain B_xO_y-type molecules besides B atoms.

On the other hand, from a SIMS measurement for a grown film with 8×10^{18} cm^{-3} carrier concentration, oxygen content in the boron-doped sample was found to be lower than 10^{18} cm^{-3}. This fact means that boron was not incorporated into the film as B_xO_y molecules. Oxygen atoms seem to re-evaporate from substrate surface by the reaction with arriving silicon atoms to form volatile SiO molecules.

Detailed study on boron evaporation mechanism from B_2O_3 source and on oxygen desorption from a growing surface is needed.

In conclusion, using a B_2O_3 source in usual K-cell, boron doping has been easily realized up to 7×10^{19} cm^{-3}. Oxygen content in grown films was lower than one tenth of boron content. Carrier concentration was independent of substrate temperature and was proportional to the inverse of growth rate. Impurity profile was sufficiently steep.

Acknowledgements

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