

Ultra-Shallow and Abrupt Boron Profiles in Si by the δ -Doping Technique

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Ultra-shallow and abrupt Boron (B) profiles in Si are achieved by using molecular beam epitaxy, and thermal stability of these profiles is closely examined. Oxidation enhanced diffusion of δ -doped B can be minimized by wet O_2 oxidation owing to the shorter oxidation time than that of dry O_2 . Sheet resistance of heavily δ -doped layers is $1 \text{ k}\Omega/\text{sq}$ which is almost constant even after thermal annealing. This value is about 1/10 the reported value obtained by solid phase diffusion in which solid solubility limits the maximum carrier concentration.

1. Introduction

Precise control of Boron (B) profiles in Si is becoming increasingly important in the formation of ultra-shallow source/drain junctions⁽¹⁾ for p-MOSFETs, and for punch-through stopper⁽²⁾ in n-MOSFETs, as illustrated in Fig.1. Such junctions are usually formed by ion implantation which is highly controllable in a wide range of doping concentrations. However, scattering and channeling of dopant ions in Si crystal result in relatively broad depth profiles. Recently, solid phase diffusion from Boron silicated glass or Boron molecular layer has been investigated for ultra-shallow junction formation⁽¹⁾⁽³⁾. These techniques, however, suffer from solid solubility limitation which determines the maximum carrier concentration. Thus, ultra-shallow B junctions with low resistivity are difficult to form.

Molecular beam epitaxy (MBE) is a promising technique for dopant confinement on an atomic scale (δ -doping) and for precise control of a wide range of doping concentrations. While many studies of B δ -doping have been reported⁽⁴⁾, the thermal stability of B δ -doped layers, which is indispensable in device fabrication, has not been investigated. In this paper, two important considerations in the formation of δ -doping profiles will be discussed: oxidation enhanced diffusion (OED)⁽⁵⁾ during gate oxidation, and B precipitation due to solubility⁽⁶⁾.

2. Experimental

Vacuum Generator 366 system was used for Si MBE. This system contains an electron beam gun

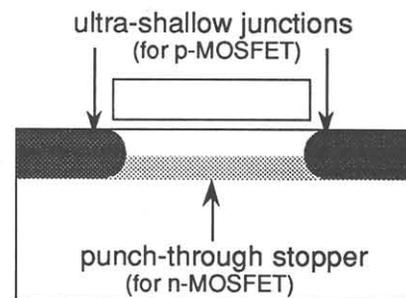


Fig.1 Schematic cross section of δ -doped B punch-through stopper for n-MOSFETs and ultra-shallow junctions for p-MOSFETs.

evaporator for Si deposition and an HBO_2 effusion cell for B doping. Si (100) wafers were precleaned by chemical treatment and a thin protective oxide layer was formed. Then, the oxide layer was sublimated in the MBE chamber by heat treatment at 830°C for 20 min⁽⁷⁾.

The samples for thermal diffusion experiments were formed as follows. The 200-nm-thick Si buffer layer was grown on a p-type Si ($9\text{-}12 \Omega \text{ cm}$) substrate and then HBO_2 was adsorbed on it at 600°C . Next, a 180-nm-thick Si cap layer was grown at 500°C with growth rate of 0.1 nm/sec, which is low enough to suppress surface segregation of B⁽⁸⁾. As a result, B is confined within the buried 3-nm-thick region of Si. Furnace annealing at around 800°C was performed in inert and oxidizing ambients. Capacitance-voltage (C-V) measurements were used to examine the B profiles. Schottky contacts 0.4mm in diameter were formed by Ti evaporation. It should be noted that Boron sheet density was

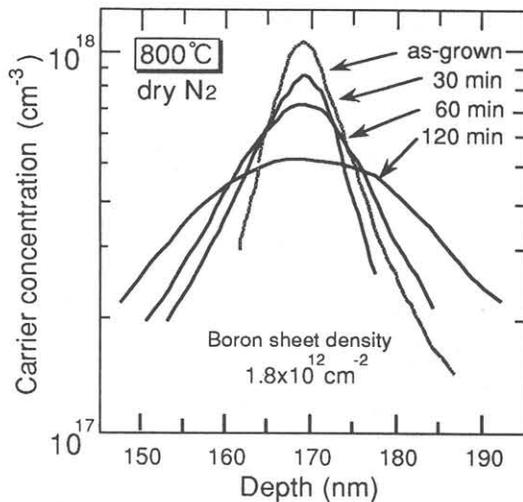


Fig.2 Carrier profiles of δ -doped Boron layer annealed in dry N₂.

selected to be $1.8 \times 10^{12} \text{ cm}^{-2}$ to prevent avalanche break down⁽⁹⁾.

Heavily δ -doped samples were formed as follows. HBO₂ was adsorbed on an n-type Si (8-12 $\Omega \text{ cm}$) substrate. Then, 5-nm- or 100-nm-thick Si cap layer was grown to incorporate B into substitutional site. Furnace annealing at 600°C and 800°C and rapid thermal annealing at 1000°C, were used to investigate the thermal stability of δ -doped B in inert ambient. Secondary ion mass spectroscopy (SIMS) was used to investigate the B depth profiles, and sheet resistivity was measured by the four-point probe technique.

3. Results and discussion

Figure 2 shows the carrier profiles obtained by C-V measurement after annealing in dry N₂ at 800°C. It was found that these profiles can be approximated by Gaussian distribution. Generally, a carrier profile is different from a dopant profile in the case of non-uniform doping. However, it was confirmed by computer simulation that the standard deviation (σ) of the Gaussian profile of the dopant can be estimated well from the carrier profile⁽¹⁰⁾. It was also found that the dispersion value (σ^2) of the carrier profile as a function of annealing time (t) follows the theoretical relation for a Gaussian distribution: $\sigma^2 = \sigma_0^2 + 2Dt$ (D ; diffusion coefficient). Arrhenius plots of the diffusion coefficient of B in inert and oxidizing ambients are shown in Fig. 3. As can be clearly seen, OED occurs in this low temperature range, and the diffusivity in wet O₂ is higher than that in dry O₂. It is well known that OED is caused by Si interstitials generated at the SiO₂/Si interface⁽⁵⁾. In our case, it was shown that the differences between dry O₂ and wet O₂ can be attributed to the differences in oxidation rates which determine the

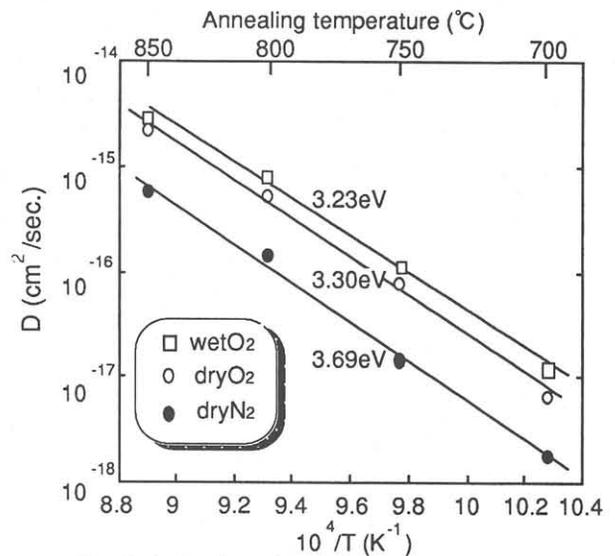


Fig.3 Arrhenius plots of diffusion coefficients of δ -doped Boron.

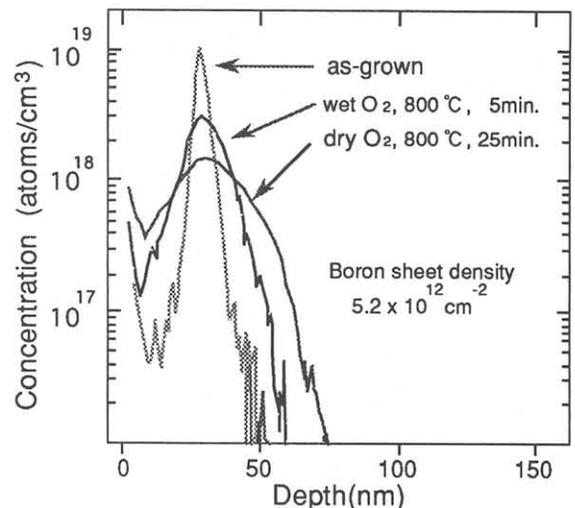


Fig.4 Boron SIMS profile after 5-nm-thick oxide growth in wet O₂ at 800°C.

concentration of Si interstitials. Figure 4 shows the B depth profile after growing a 5-nm-thick oxide layer at 800°C in wet O₂. Since the oxidation rate in wet O₂ is faster than that in dry O₂, the diffusion length ($= \sqrt{2Dt}$) in wet O₂ is smaller than that in dry O₂ in spite of higher diffusivity. As a result, the abrupt B profile for a punch-through stopper can be minimized ($\sigma \sim 7.5 \text{ nm}$) by using wet O₂ ambient during gate oxidation.

Figure 5 (a) shows the SIMS depth profiles of heavily δ -doped B layers with sheet densities of 1×10^{14} and $3 \times 10^{14} \text{ cm}^{-2}$ after dry N₂ annealing at 800°C. The thickness of Si cap layer was 100 nm for SIMS measurement. The profiles remain abrupt even after 30 minutes of annealing, which corresponds to a junction depth of 22 nm at $1 \times 10^{18} \text{ cm}^{-3}$. In addition, the profiles maintain Gaussian distribution without shoulders, which means that there is no B precipitation due to solubility. In contrast, as shown in Fig. 5 (b), the sample formed by solid phase

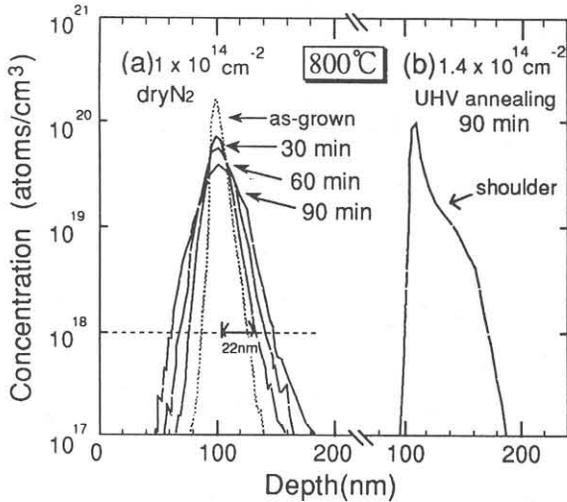


Fig.5 SIMS profiles of heavily doped Boron (a) δ -doped B annealed in dry N₂, (b) Solid phase diffused B by UHV annealing.

B diffusion in the Si-MBE chamber shows a shoulder due to B solubility of $3 \times 10^{19} \text{ cm}^{-3}$ at 800°C ⁽⁴⁾.

Sheet resistance (ρ_s) of δ -doped B with a 5-nm-thick Si cap layer is shown in Fig. 6 as a function of annealing time at 1000°C , 800°C , and 600°C in dry N₂. At 800°C , ρ_s is 2.3 and 1.1 $\text{k}\Omega/\text{sq}$. for B sheet densities of 1×10^{14} and $3 \times 10^{14} \text{ cm}^{-2}$, respectively. These values are in good agreement with data obtained by Hall measurement ⁽¹¹⁾. The ρ_s values are almost constant even after the annealing, and are less than 1/10 that of samples formed by solid phase diffusion having the same junction depth ($x_j \sim 10 \text{ nm}$) ⁽⁹⁾. In addition, an increase in sheet resistance was observed at 600°C . It is suggested, then, that B precipitation occurred before any significant broadening of depth profile at this low temperature.

4. Conclusions

Abrupt Boron profiles in Si can be formed using the δ -doping technique. Oxidation enhanced diffusion occurs in the temperature range of $700\text{--}850^\circ\text{C}$ and diffusivity in wet O₂ is larger than that in dry O₂ owing to a higher oxidation rate. The profiles in Si can be maintained after gate oxidation in wet O₂ but not in dry O₂ in spite of higher diffusivity.

An ultra-shallow, B-doped layer with low resistance was also shown to be easily obtainable. Sheet resistance of heavily δ -doped layers is 1/10 that of samples formed by solid phase diffusion, and are almost constant, even after annealing at 800°C and 1000°C . At 600°C , sheet resistance increases with increasing annealing time. Therefore, it is believed that B precipitation occurred before any significant broadening of depth profile at this low temperature.

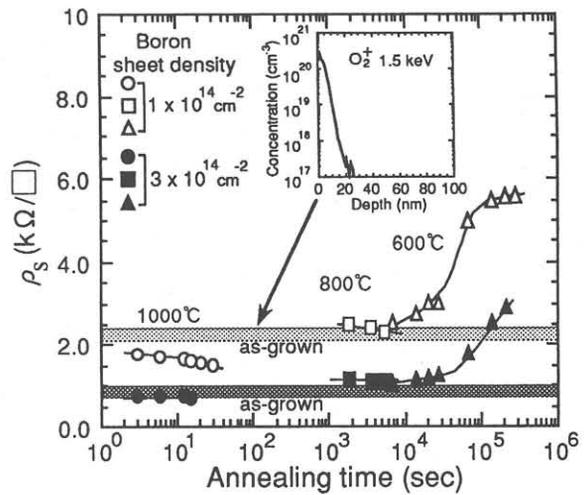


Fig.6 Sheet resistance of δ -doped B as a function of annealing time.

Acknowledgments

The authors would like to thank Drs. Kiyokazu Nakagawa and Eiji Takeda for their fruitful discussion and continuous encouragement throughout this study.

References

- (1) J. Nishizawa, K. Aoki and T. Akamine, *Appl. Phys. Lett.* 56 (1990) 1334.
- (2) K. Nakagawa, A. A. Gorkum and Y. Shiraki, *Appl. Phys. Lett.* 54 (1989) 1869.
- (3) M. Saito, T. Yoshitomi, H. Hara, M. Ono, Y. Akasaka, H. Nii, S. Matsuda, H. S. Momose, Y. Katsumata, Y. Ushiku and H. Iwai, *IEEE Trans. Electron Devices* 40 (1993) 2264.
- (4) N.L. Matthey, M. Hopkinson, R.F. Houghton, M. G. Dowsett, D. S. McPhail, T. E. Whall and E. H. C. Parker, *Thin Solid Films* 184 (1990) 15.
- (5) K. Taniguchi, K. Kurosawa and M. Kashiwagi, *J. Electrochem. Soc.* 127 (1980) 2243.
- (6) C. P. Parry, R. A. Kubiak, S. M. Newstead, T. E. Whall and E. H. C. Parker, *J. Appl. Phys.* 71 (1992) 118.
- (7) A. Ishizaka and Y. Shiraki, *J. Electrochem. Soc.* 133 (1986) 666.
- (8) E. Murakami, H. Kujirai and S. Kimura, *Ext. Abst. 1993 SSDM* p. 216.
- (9) S. M. Sze, *Physics of Semiconductor Devices*, (1981)
- (10) H. Kujirai, E. Murakami and S. Kimura, unpublished.
- (11) H. J. Gossmann and F. C. Unterwald, *Phys. Rev. B* 47 (1993) 12618.