

Study of Boron-Doped nm-Deep Junctions Fabricated by B₂H₆ Surface Reaction Doping

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Abstract—Doping reaction of diborane B₂H₆ on Si(100) substrates in an atmospheric pressure chemical vapor deposition (APCVD) system has been studied in terms of dopant profile and junction depth as a function of gas source exposure. Since effective p⁺-type doping is achieved within few nanometers from the surface, the characterization of these extremely ultra-shallow junctions requires to supplement the experimental data obtained by secondary ion mass spectrometry (SIMS) with process simulations, capacitance-voltage profiling and sheet resistance measurements. This approach can overcome the limitations of low depth resolution due to the conditions of the surface analytical technique and provide more insight into the mechanisms involved in the doping process.

Index Terms—Boron, capacitance-voltage measurement, chemical vapor deposition (CVD), junction depth, secondary ion mass spectrometry (SIMS), sheet resistance measurement.

I. INTRODUCTION

AS vertical dimensions of semiconductor devices target the sub-10-nm scale, new challenges are imposed both to doping technologies and measurement techniques for accurate and reliable characterization of dopant profiles and junction depths. Future doping technology could mainly benefit from surface reaction methods [1], such as molecular layer doping (MLD) [2], rapid vapor-phase direct doping (RVD) [3], that do not suffer from limitations of traditional implantation and offer good controllability of impurity concentration to form ultra-shallow junctions. In an earlier paper, we have also presented a novel doping process that forms boron-adsorbed layers on the silicon surface [4]-[5]. By decomposition of diborane B₂H₆ in an atmospheric pressure chemical vapor deposition (APCVD) system at 700 °C, effective B-doping of the silicon substrate within few nanometers is achieved and this results in high-quality and extremely ultra-shallow p⁺-n junctions.

On the other hand, for such nm-deep junctions advanced measurement techniques to characterize the doping profile are also required. Harrington *et al.* [6] have illustrated the capabilities of 2-keV-O₂⁺ secondary ion mass spectrometry (SIMS) for B profiling and the limitations for junction depths

less than 30 nm, although more aggressive depth resolution conditions have been demonstrated to be used in [7] for sub-10-nm B-doped layers. However, Ortiz *et al.* [8] have recently proposed a technique based on a capacitance-voltage doping profiling to determine with high accuracy very shallow and abrupt surface boron profiles, providing great advantages compared to destructive and complex analytical techniques such as SIMS. Therefore, combining data from both analytical and electrical measurement techniques can result in an improved characterization of the ultra-shallow junctions and provide a better understanding of the phenomena involved in the doping process.

In this work, we report on the application of measurement techniques to further characterize the B adsorption on Si during B₂H₆ surface reaction doping. In particular, secondary ion mass spectrometry (SIMS), capacitance-voltage profiling and sheet resistance measurements have been used to measure B profiles and to determine the junction depth and the electrical activation of dopant in the surface boron-doped silicon.

II. SECONDARY ION MASS SPECTROMETRY (SIMS)

N-type 2-5 Ωcm Si(100) wafers have been used as the substrates. After a treatment with conventional cleaning and HF dipping, an *in-situ* thermal cleaning step has been performed in H₂ ambient at 900 °C for 30 min in order to remove native oxide on the silicon surface. Then, diborane B₂H₆ is introduced into the APCVD reactor chamber with hydrogen as the carrier gas. The exposure has been carried out at 700 °C for times varying from 1s to 10 min. Finally, in order to get an accurate SIMS signal from the surface, a 100-nm-thick layer of amorphous silicon has been sputtered at room temperature on the samples after the boron deposition.

The boron profiles have been analyzed by using 2-keV-O₂⁺ primary ions with an incident angle of 45°, and they are shown in Fig. 1. Although the analysis conditions can generally provide accurate measurement of B dose, the depth resolution for such ultra-shallow junctions is insufficient. In particular, the exponential decay of boron profiles in the substrate has been suggested to be caused not by diffusion of boron, but by the knock-on effect of the oxygen ions during SIMS analysis on the B atoms [6], [9]. The impact of SIMS cascade mixing on ultra-shallow junction formed with a low energy ion implantation has been demonstrated to significantly affect the

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profile tailing. In fact, the expected depth of ~ 3 nm at a boron concentration of 10^{18} cm^{-3} differed from the value of ~ 12 nm obtained from SIMS analysis [6]. It is interesting to note that the latter depth is similar to the SIMS value for B profile formed after 1 s deposition. However, both the extremely short exposure time and the relatively low processing temperature (700°C) would not be able to determine such a deep diffusion into the Si substrate.

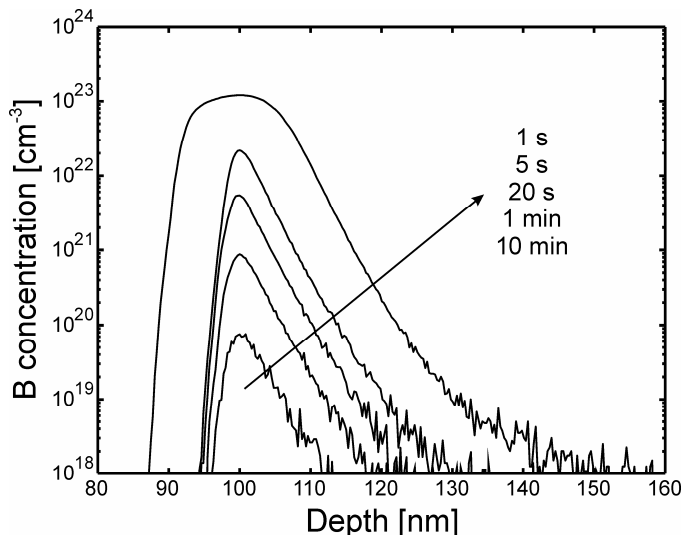


Fig. 1. Boron SIMS profiles for 1 s to 10 min B_2H_6 exposure at 700°C . The samples are covered with 100 nm PVD α -Si. The point of peak B concentration is moved to 100 nm in all cases.

Finally, assuming a similar knock-on effect induced on the B atoms, 2-keV- BF_2^+ implantations with an incident angle of 45° and doses similar to the as-deposited B layers have been simulated with Taurus TSUPREM-4TM software [10]. The comparison of corresponding B profiles is shown in Fig. 2.

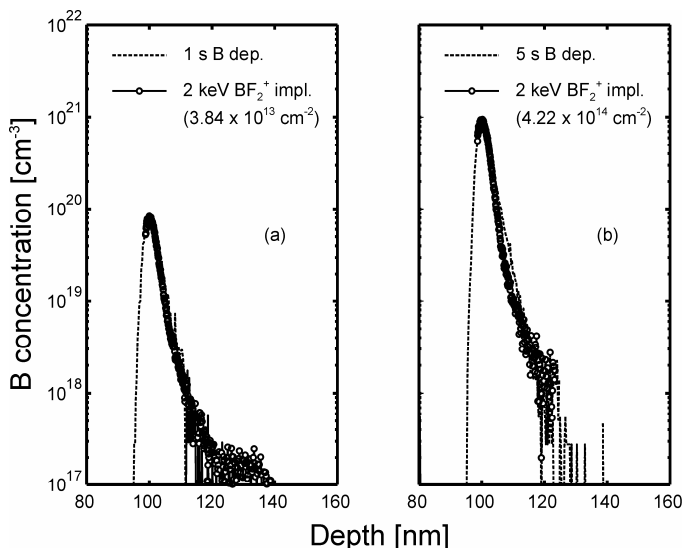


Fig. 2. Impact of SIMS knock-on effect on B profile tailing: comparison of as-deposited B-layer profiles after 1 s (a) and 5 s (b) B_2H_6 exposure at 700°C with BF_2^+ implantations, simulated under comparable SIMS conditions.

The agreement between measured and simulated data confirms that the profile tailing induced by the oxygen primary ion beam might dominate the experimental profiles.

III. CAPACITANCE-VOLTAGE MEASUREMENT

The diffusion of B into the substrate has been therefore monitored by a capacitance-voltage profiling technique that uses an abrupt n^+ buried layer to profile the tail of B-doped layers at the wafer surface, as described in [8]. A schematic cross-section of the test structures is shown in Fig. 3. The epitaxial $n^-p^-n^+$ layer stack has been grown on n -type 2-5 Ωcm Si(100) substrate. Shallow trenches have been formed to isolate the structures with and without B deposition. Then an LPCVD TEOS oxide surface isolation layer has been deposited in which the contact windows to be treated with a B deposition were plasma etched with soft landing on the Si. The B_2H_6 exposure has been carried out at 700°C for 30 min. The B-treated contact windows were directly covered by an Al/Si(1%) PVD metallization and contact to the neighboring structure has been then opened and metallized. After back-side metallization and front-side metal patterning, a 400°C alloy step in forming gas has been performed.

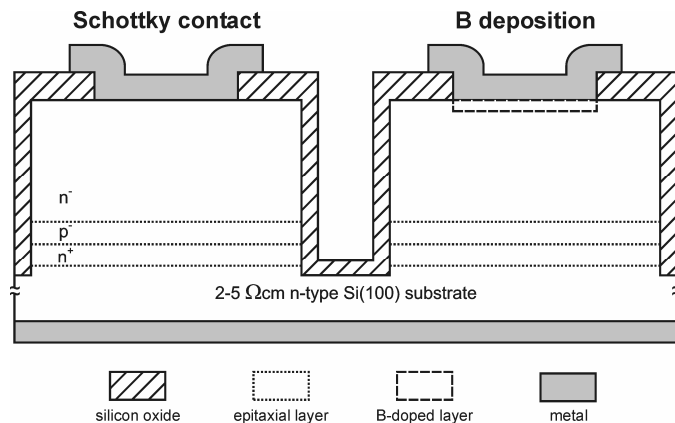


Fig. 3. Schematic cross-section of the test structures fabricated for the capacitance-voltage doping profiling technique [8].

In Fig. 4, the measured profile of the $p^-n^-p^-n^+$ structure with B deposition is compared to that of $n^-p^-n^+$ with the Schottky contact. The difference in depth (~ 10 nm) confirms that the diffusion of B atoms into the substrate is negligible at the processing temperature of 700°C . In addition, even after such a long B_2H_6 exposure, the measured value is smaller than the SIMS depth for 1 s B deposition, and this further illustrates the limitations of the analytical technique.

IV. SHEET RESISTANCE MEASUREMENT

A valuable parameter for the characterization of the doping profiles is the sheet resistance ρ_s . In fact, since the B content determined by the SIMS analysis might differ from the carrier concentration, ρ_s can indicate the electrical activation of

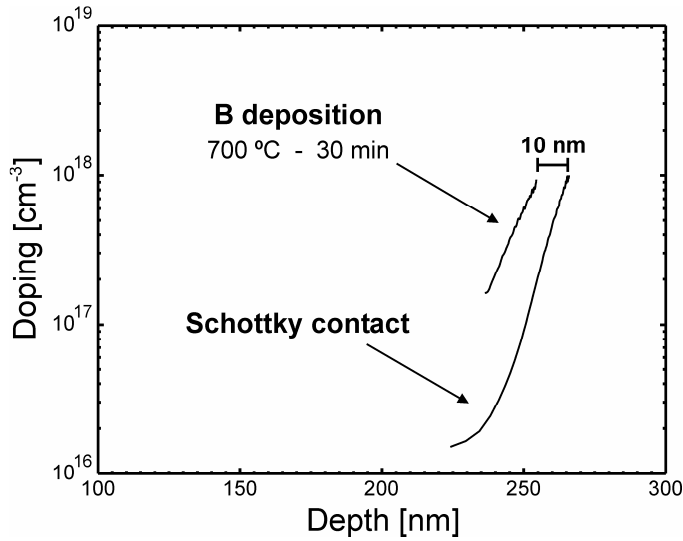


Fig. 4. C-V doping profiles measured from the abrupt n^+ buried layer to a Schottky contact and a 30 min B deposition at 700 °C.

dopants. A large variety of the current state-of-the-art non-penetrating/non-contacting tools have been investigated in [7] for sheet resistance measurement. However, both the complexity of these techniques and still their limitations for few-nm-deep junctions can make these methods unattractive. On the other hand, ρ_s can be directly determined by using differential electrical measurements on ring test structures, whose schematic cross-section is shown in Fig. 5. The structures consist of two concentric ring contacts onto regions which act as source and drain. These regions have been formed with a high dose B implantation into the n -type 2-5 Ωcm Si(100) substrate followed by long thermal annealing in order to reduce both the contact and sheet resistance beneath the metal. The resistive “channel” path between source and drain is then provided by the B-layer that has been deposited as described above, and results are reported below for samples with 10 min exposure time.

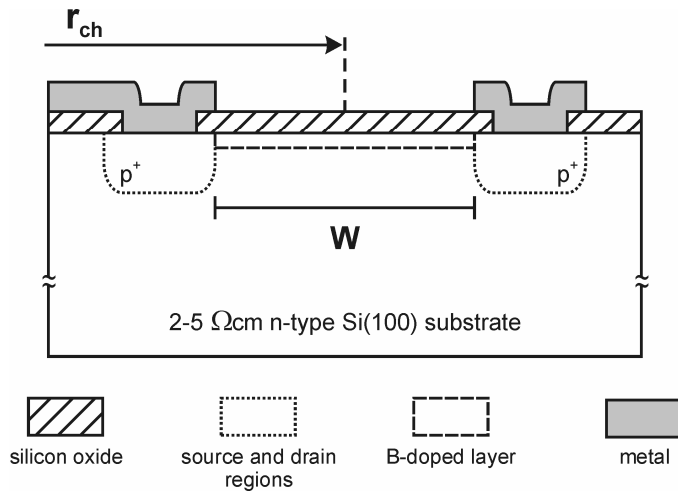


Fig. 5. Schematic cross-section of the ring test structures fabricated for the sheet resistance measurement.

The test structures have been designed with a constant radius $r_{\text{ch}} = 68.5 \mu\text{m}$ to the center of the p^+ channel and varying the distance $W (= 5, 6, 8, 10, \text{ and } 14 \mu\text{m})$ between source and drain. Therefore, to extract the sheet resistance a differential measurement technique can be applied to eliminate parasitic series resistance components. A linear approximation can be made since the condition $r_{\text{ch}} \gg W$ is satisfied [11]-[12]. The total measured resistance is thus given by

$$R_T = R_S + R_D + R_{\text{boron-layer}} = K + \frac{\rho_s}{2\pi r_{\text{ch}}} W \quad (1)$$

where R_S and R_D represent the source and drain contact resistances, respectively, which are assumed here to be constant. As shown in Fig. 6, the linear dependence on the spacing W is observed, and ρ_s can be determined by the slope of the line interpolating the measured data. Thus, the sheet resistance for B-layer formed at 700 °C for 10 min is $1.04 \times 10^4 \Omega/\text{sq}$.

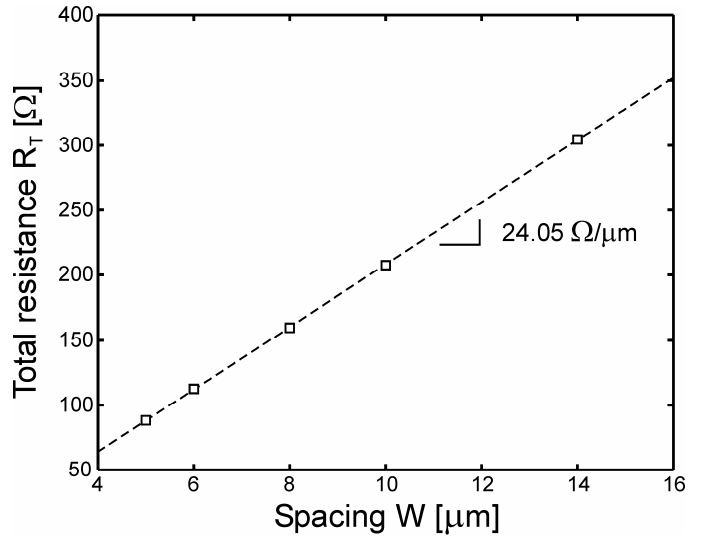


Fig. 6. Total resistance R_T as function of source-drain spacing W . The sheet resistance ρ_s of the B-layer deposited at 700 °C for 10 min is extracted from the slope of the line interpolating the measured data.

Although the SIMS doping concentrations exceed the boron solid solubility of $\sim 2 \times 10^{19} \text{ cm}^{-3}$ at 700 °C, the sheet resistance measurement indicates that the incorporation of B atoms into the substrate appears to be not completely substitutional. In fact, the corresponding boron dose determined from ρ_s with bulk silicon mobility of $50 \text{ cm}^2/\text{Vs}$ is $1.2 \times 10^{13} \text{ cm}^{-2}$, which is lower than $9.16 \times 10^{13} \text{ cm}^{-2}$ from SIMS data [5].

Finally, this method in combination with an HNO_3 cleaning step and HF dipping, which can be performed after B deposition, provides further insight into the junction depth. The removal of the resulting ultra-thin cleaning oxide has been measured to significantly increase the sheet resistance. In particular, for exposure time shorter than 5 min the p^+ channel

B-layer is substantially removed. These results confirm that our B deposition process is suitable for formation of nm-deep junctions in silicon.

V. CONCLUSION

In summary, we have applied different measurement techniques to characterize the extremely ultra-shallow p^+n junctions formed by B adsorption on Si during B_2H_6 surface reaction doping in terms of dopant profiles and junction depth.

It has been shown that due to the large amount of deposited B atoms in our CVD process a SIMS profile does not give sufficient depth resolution to be able to isolate whether there is B diffusion into the substrate. In fact, the knock-on effect of oxygen ions dominates the experimentally measured profiles. On the other hand, accurate measurement of junction depth is achieved with a dedicated capacitance-voltage profiling technique that confirms effective boron doping to occur within 10 nm from the silicon surface for long B_2H_6 exposure time. Finally, measurement of the sheet resistance has been used to determine the electrical activation of dopants in the as-adsorbed B-layers, which is mainly limited by the solid solubility at the processing temperature.

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REFERENCES

- [1] Y. Kiyota, "Surface reaction doping using gas source for ultra shallow junctions," in *Ext. Abstr. 1st IEEE Int. Workshop on Junction Technology (IWJT)*, Tokyo, Japan, 2000, pp. 19–22.
- [2] J. Nishizawa, K. Aoki, and T. Akamine, "Ultrashallow, high doping of boron using molecular layer doping," *Appl. Phys. Lett.*, vol. 56, no. 14, pp. 1334–1335, April 1990.
- [3] Y. Kiyota, T. Nakamura, T. Inada, A. Kuranouchi, and Y. Hirano, "Characteristics of shallow boron-doped layers in Si by rapid vapor-phase direct doping," *J. Electrochem. Soc.*, vol. 140, no. 4, pp. 1117–1121, April 1993.
- [4] F. Sarubbi, L. K. Nanver, and T. L. M. Scholtes, "CVD delta-doped boron surface layers for ultra-shallow junction formation," in *Advanced Gate Stack, Source/Drain, and Channel Engineering for Si-Based CMOS 2: New Materials, Processes, and Equipment, 210th Meeting of The Electrochemical Society*, Cancun, Mexico, 2006, *ECS Transactions*, vol. 3, no. 2, pp. 35–44.
- [5] F. Sarubbi, L. K. Nanver, and T. L. M. Scholtes, "Uniformity of chemical vapor deposited boron-silicide layers on silicon," in *Proc. 9th Annual Workshop on Semiconductor Advances for Future Electronics and Sensors (SAFE)*, Veldhoven, The Netherlands, 2006, pp. 479–482.
- [6] W. L. Harrington, C. W. Magee, M. Pawlik, D. F. Downey, C. M. Osburn, and S. B. Felch, "Techniques and applications of secondary ion mass spectrometry and spreading resistance profiling to measure ultrashallow junction implants down to 0.5 keV B and BF_2 ," *J. Vac. Sci. Technol. B*, vol. 16, no. 1, pp. 286–291, January/February 1998.
- [7] T. Clarysse, A. Moussa, F. Leys, R. Loo, W. Vandervorst, M. C. Benjamin, R. J. Hillard, V. N. Faifer, M. I. Current, R. Lin, and D. H. Petersen, "Accurate sheet resistance measurement on ultra-shallow profiles," in *Proc. Doping Engineering for Device Fabrication, Symposium of Materials Research Society (MRS)*, San Francisco, CA, USA, 2006, vol. 912, pp. 197–202.

- [8] C. J. Ortiz, L. K. Nanver, W. D. van Noort, T. L. M. Scholtes, and J. W. Slotboom, "CV doping profiling of boron out-diffusion using an abrupt and highly doped arsenic buried epilayer," in *Proc. 15th Int. Conf. on Microelectronic Test Structures (ICMTS)*, Cork, Ireland, 2002, pp. 83–88.
- [9] Y. Kiyota, T. Nakamura, and T. Inada, "Boron δ -doping in Si using atmospheric pressure CVD," *Appl. Sur. Sci.*, vol. 82/83, pp. 400–404, December 1994.
- [10] Taurus TSUPREM-4TM version W-2004.09 *User Guide*, Synopsys, Inc..
- [11] S. B. Evseev, L. K. Nanver, and S. Milosavljević, "Ring-gate MOSFET test structures for measuring surface-charge-layer sheet resistance on high-resistivity-silicon substrates," in *Proc. 19th IEEE Int. Conf. on Microelectronic Test Structures (ICMTS)*, Austin, TX, USA, 2006, pp. 3–8.
- [12] G. K. Reeves, "Specific contact resistance using a circular transmission line model," *Solid-State Electron.*, vol. 23, no. 5, pp. 487–490, May 1980.