Recoil implantation method for ultrashallow p^+/n junction formation

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A recoil implantation technique is investigated for ultrashallow p^+/n junction formation. In this method, a 3–35 nm thick B layer is deposited on the wafer by magnetron sputtering. Then a medium energy (10–40 keV) Ge implant drives the boron atoms into Si by means of ion beam mixing. The remainder of the boron film is chemically etched away prior to the annealing step. Sub-60 nm deep p^+/n junctions with sheet resistance less than 1000 Ω/sq and test diodes with leakage current density below 2 nA/cm² have been formed using this method. © 2000 American Institute of Physics. [S0021-8979(00)02004-1]

I. INTRODUCTION

Ultrashallow p^+/n junction formation is one of the most difficult challenges for deep submicron complementary metal–oxide–semiconductor (CMOS) technology.¹ This results from the long projected range of the implanted B⁺ ions, boron channeling, and rapid boron diffusion. In addition, low beam current at low implantation energy makes it even more difficult to realize shallow boron doping with conventional ion implanters. The use of implantation with molecular species such as BF₂⁺ and B₁₀H₁₄⁺ reduces the penetration of boron into the substrate. However, fluorine helps boron, from the polysilicon gate, penetrate the gate oxide and enter the channel region.² Additionally, a better ion source needs to be developed for B₁₀H₁₄⁺ implantation to prevent the cluster ions from cracking before reaching the wafer.³

In this study, we investigated a recoil implantation process for shallow boron doping. In this method, a boron layer is first deposited onto the Si wafer by magnetron sputtering. Then a medium energy (10–40 keV) Ge implant drives the boron atoms into Si by means of ion beam mixing. The boron layer remaining on the surface is chemically etched away before the rapid thermal anneal (RTA) step that activates the dopant. The advantage of this process is high throughput because medium energy Ge implantation is used instead of ultralow energy (subkilo electron volts) B implantation, and conventional ion implanters have much higher beam current at medium energy than at low energy.

Ge was selected as the ion species to knock B into Si for a number of reasons. Ge has been the favorite choice for pre-amorphization of Si to avoid B channeling, because Ge has the advantage of heavy mass.⁴ Ge was reported to result in lower sheet resistance than other pre-amorphization choices, such as Si, Ar, and F.⁵ In addition, Ge has an infinite solid solubility in Si, and is probably not detrimental to the performance of silicon devices.

A systematic approach was conducted to investigate this new recoil implantation process. First, the purity of the deposited B layer was confirmed. Then the effects of the process parameters, such as Ge energy, Ge dose, B layer thickness, and anneal temperature, on the recoil B profiles and sheet resistance were characterized and analyzed. The experimental results were compared to simulated predictions of as-implanted Ge and B profiles. In addition, electrical properties of the junctions were also studied.

II. EXPERIMENT

Two categories of samples were used in this study. Unpatterned wafers were used to characterize the material properties of the junctions, such as the B profiles and sheet resistance. Test diodes were fabricated to study the electrical properties of the junctions.

Unpatterned n -type $\langle 100 \rangle$ Si wafers with a resistivity higher than 500 $\Omega\text{-cm}$ were used to study the material properties. The high resistivity of the substrate facilitate accurate four-point probe measurements. While the probes will likely pass through the thin junction region, the probe-to-probe current will still be concentrated in the thin highly-doped regions. The wafers were first cleaned with buffered HF solution. The boron layers, with thicknesses ranging from 3 to 35 nm, were deposited on the Si wafers with radio frequency (rf) magnetron sputtering using a solid 99.5% pure B target. The thicknesses of the B films thicker than 10 nm were measured by profilometry, while the thicknesses of the B films thinner than 10 nm were estimated from the measured deposition rate. ⁷⁴Ge⁺ was implanted at 20 or 40 keV at 7° with a dose of 3×10^{14} or $1 \times 10^{15} \text{ cm}^{-2}$. Following the implantation, the remainder of the boron layer was etched away by a hot nitric acid dip.⁶ The samples were annealed at 950 or 1050 °C for 10 s in Ar ambient in a Minipulse (AG Associates) chamber with a ramp-up rate of 25 °C/s. The chemical composition of the deposited B layer was characterized by Auger electron spectroscopy (AES). The sheet resistance was measured by the standard four-point technique with a probe tip radius of 5 mils. The boron and Ge profiles were mea-

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FIG. 1. Atomic concentration profiles of a high purity 10 nm thick deposited B layer on Si.

sured by secondary ion mass spectrometry (SIMS) simultaneously. The SIMS was performed on a Physical Electronics Model 6600 Spectrometer using 2 keV oxygen primary ion bombardment under oxygen leak.

The test diodes were fabricated on *n*-type $\langle 100 \rangle$, 1–10 Ω -cm, Si wafers. The wafers were first cleaned using a standard Radio Corporation of America (RCA) clean process.⁷ Then a 500 nm thick thermal oxide was grown, and round contact holes with a diameter of 500 μ m were opened in the oxide. Next, a 15 nm thick B layer was deposited, and the wafer was implanted by 40 keV, 10^{15} cm^{-2} Ge⁺. After implantation, the remaining B layer was removed by hot nitric acid. The junction was annealed at 950 °C for 10 s. Then a 700 nm thick Al–1% Si film was deposited, patterned, and annealed at 410 °C for 20 min in forming gas.

TAMIX, a Monte Carlo code,⁸ was used to simulate the as-implanted Ge and B profiles, as well as the damage density profiles or the distributions of energy loss due to nuclear collisions in Si induced by Ge implantation. In the simulations, the density of the boron layer was assumed to be 2.35 g/cm³, the density of bulk B.⁹ The displacement energy and surface binding energy of boron were assumed to be 25 and 5.7 eV, respectively. The displacement energy of Si was assumed to be 15 eV. 10 000 ions were traced for each simulation.

Monte Carlo simulations were also performed to predict the depths of the amorphous Si layers formed by the Ge implants. First, the threshold damage density (TDD) for amorphization of Si by Ge⁺ was derived by correlating the measured depths of amorphous Si layers created by 15 and 27 keV Ge implants, reported in Ref. 4, to the corresponding damage density distributions calculated by TAMIX.¹⁰ The TDD values thus derived was about $2.0 \times 10^{20} \text{ keV/cm}^3$, consistent for both cases. Then this TDD value was used to predict the depths of the amorphous Si layers in this study.

III. RESULTS AND DISCUSSION

A. High purity B film

The deposited B layer must be pure enough to prevent the incorporation of undesirable impurities into Si during the recoil implantation. AES measurement demonstrates that the deposited B layer is more than 95% pure (Fig. 1). Small amounts of C and O were also observed at the surface. It is

FIG. 2. B profiles for 20 keV Ge recoil implantation and B⁺ implantation at 0.5 and 20 keV. The latter two cases were based on the information published in Refs. 11 and 12, respectively.

possible that these contaminants were introduced during the transportation step between the deposition chamber and the AES system.

During the Ge implantation, some of the surface B atoms are also sputtered off. If the Ge dose is too high, the sputtering might deplete the dopant. The TAMIX program was used to study the sputtering rate of boron by Ge⁺. The surface recession of B layer caused by 40 keV, 10^{15} cm^{-2} Ge⁺ is numerically calculated to be 0.6 nm, which is small compared to the original thickness of the deposited B layer (3–35 nm). Therefore, sputtering of the boron during the Ge implant is assumed to be insignificant.

B. As-recoiled B profiles

This recoil implantation method results in a much shallower B profile than direct B⁺ implant does at the same implantation energy. Figure 2 compares the experimental as-implanted B profiles formed by 0.5 and 20 keV B⁺ with the as-recoiled B profile formed by 25 nm thick B deposition and 20 keV, 10^{15} cm^{-2} Ge⁺ implantation. The B profile formed by 20 keV recoil implantation is much shallower than the one formed by 20 keV B⁺, and is almost as shallow as the B profile formed by 0.5 keV B⁺. The as-recoiled B profile has a shape similar to an exponentially decaying function rather than the Gaussian shape of the typical as-implanted B profiles formed by B⁺ implant. TAMIX simulations were also performed to predict the as-implanted B and Ge profiles. The simulation results agree well with the SIMS profiles (Fig. 3).

The recoil B profile is shallow because the recoil B atoms receive only a fraction of the original implantation energy. During implantation, the energetic Ge ions collide with the boron atoms, and transfer energy to the recoil B atoms. The recoil B atoms, in turn, transfer energy to more atoms while traveling in the substrate. The maximum energy transfer ratio γ for a two-atom collision is about $4M_1M_2/(M_1 + M_2)^2$, where M_1 and M_2 are, respectively, the mass of the incident atom and the recoil atom.¹³ When the incident ⁷⁴Ge collides with ¹¹B, γ is about 0.45. Therefore, the maximum energy can be transferred to B atom is less than half of the original Ge energy. In addition, the scattering cross section decreases as the transferred energy is increased. As a result, most of the B atoms knocked away by Ge receive much

FIG. 3. Simulated and experimental profiles of (a) Ge and (b) boron for 7.5 nm thick B deposition and 20 keV, $1 \times 10^{15} \text{ cm}^{-2}$ Ge implant.

lower energy than that maximum value. Moreover, the collision between Ge and B is a rare event, compared to the secondary collision between the recoiled B atom and another B atom, which involves even lower energy transfer. Consequently, B atoms will not be knocked into Si very far, even with incident Ge^+ energy as high as 40 keV.

The junction depths in this study having been characterized at a boron concentration value of 10^{18} cm^{-3} . Although this concentration is higher than the doping level of the next generation of CMOS technology,¹ justification for this choice is twofold. First, for economics and expediency it was necessary to obtain the SIMS experimental data for both B and Ge concentration profiles simultaneously. As a result, the B concentration profile data below 10^{18} cm^{-3} was fairly noisy, precluding a determination of the junction depth at lower concentration levels. Hence, 10^{18} cm^{-3} was selected as the reference *n*-substrate doping level to calculate the geometric p^+/n junction depths for this article. Second, using 10^{18} cm^{-3} for the junction depth has pre-established precedent and a comparative body of literature exists using this choice.^{14,15}

C. Effects of anneal, Ge dose, and Ge energy

Low sheet resistance or high B dose is required for CMOS source and drain junctions. This in turn demands a sufficient Ge dose to knock enough B atoms into Si in our recoil implantation process. In this study, a Ge dose of at least $3 \times 10^{14} \text{ cm}^{-2}$ is used. This dose is sufficient to amorphize the surface Si layer if the overlying B layer is thin enough. Monte Carlo simulations indicated that amorphization of Si occurred in most of the experiments described in this article. An additional advantage of amorphization is that low sheet resistance is achievable with anneal temperature as low as 550 °C.¹¹ This is caused by solid phase epitaxy (SPE) that regrows the amorphous Si into crystalline Si, and results in a very high percentage of dopant activation in the regrown Si.

Figure 4 shows the effects of anneal, Ge dose, and Ge energy on as-recoiled and annealed B profiles. The junctions

FIG. 4. SIMS profiles of B in Si after Ge implantation through a 15 nm thick B layer on Si. The process conditions were (a) 20 keV, $3 \times 10^{14} \text{ cm}^{-2}$ Ge^+ plus 950 °C RTA, (b) 20 keV, $1 \times 10^{15} \text{ cm}^{-2}$ Ge^+ , no anneal, (c) 20 keV, $1 \times 10^{15} \text{ cm}^{-2}$ Ge^+ plus 950 °C RTA, (d) 20 keV, $1 \times 10^{15} \text{ cm}^{-2}$ Ge^+ plus 1050 °C RTA, (e) 40 keV, $1 \times 10^{15} \text{ cm}^{-2}$ Ge^+ , no anneal, (f) 40 keV, $1 \times 10^{15} \text{ cm}^{-2}$ Ge^+ plus 950 °C RTA. The anneal time for all cases was 10 s.

were formed by 15 nm B layer deposition, 20 or 40 keV Ge implant at a dose of 3×10^{14} or $1 \times 10^{15} \text{ cm}^{-2}$, and an anneal at 950 or 1050 °C for 10 s.

First, the higher anneal temperature (1050 °C) results in lower sheet resistance and a deeper B profile than the lower anneal temperature (950 °C) does, under the same condition of Ge implant. For the 20 keV, $1 \times 10^{15} \text{ cm}^{-2}$ Ge implant, the 950 and 1050 °C anneal resulted in sheet resistance of 550 and 200 Ω/sq , respectively. The annealed B profiles have humps that do not appear in the as-recoiled B profiles. The B hump centered in the end-of-range (EOR) region was observed by many authors,^{4,16–22} though the microstructure and kinetics of it still remains controversial.^{21–26} The amorphous/crystalline (a/c) interfaces predicted by the TAMIX simulations are also shown in Fig. 5, which are within the vicinity of the B humps respectively.

The higher Ge energy (40 keV) results in a deeper recoil B profile because more energy is transferred to the recoil B atoms. After the 950 °C anneal, the higher Ge energy also results in a deeper and more pronounced B hump than the lower Ge energy does.

FIG. 5. Measured B dose and simulated energy deposition as functions of thickness or depth of the B layer for 20 and 40 keV, 10^{15} cm^{-2} Ge implant.

A higher Ge dose yields more B atoms knocked in, and results in lower sheet resistance. For 20 keV implantation energy, a Ge dose of 10^{15} cm^{-2} results in a B dose of $2.7 \times 10^{15} \text{ cm}^{-2}$ and sheet resistance of $550 \text{ } \Omega/\text{sq}$, while a lower Ge dose of $3 \times 10^{14} \text{ cm}^{-2}$ results in a lower B dose of $8 \times 10^{14} \text{ cm}^{-2}$ and sheet resistance of $880 \text{ } \Omega/\text{sq}$. The knocked-in B dose is roughly proportional to the Ge dose. In addition, the lower Ge dose results in a shallower and less pronounced B hump than the higher Ge energy does after the 950°C anneal.

D. B film thickness effect

The thickness of the deposited B layer affects the knocked-in B dose significantly. If the B layer is many times thicker than the projected range of Ge in boron, most of the incident Ge ions come to rest before reaching the B/Si interface, and not many recoiled boron atoms can reach the Si. On the other hand, very few B atoms are knocked into the Si, if the B layer is much thinner than the projected range of Ge in boron, which is 17 nm at 20 keV or 28 nm at 40 keV according to the TAMIX simulations. For a particular Ge energy, there is a unique B layer thickness that maximizes the B dose in Si. Since recoil implantation is dominated by the short-range relocation, most of the B atoms knocked into Si come from the region very close to the original B/Si interface. The number of B atoms crossing the B/Si interface is thus significantly affected by the likelihood of nuclear collisions near the B/Si interface, which is correlated to the damage density or nuclear energy deposited near the B/Si interface due to the Ge implant. It was previously demonstrated that the number of Sb atoms knocked from the overlaying Sb film into Si by Kr^+ is proportional to the nuclear energy deposited at the Sb/Si interface.²⁷ Therefore, it is likely that the knocked-in B dose is proportional to the energy deposited at the B/Si interface via nuclear collisions by implanted Ge ions.

Figure 5 compares the variations of the experimental knocked-in B dose and simulated deposited energy profile as functions of B layer thickness for 10^{15} cm^{-2} Ge implants at 20 and 40 keV. The B dose was estimated from the as-recoiled B SIMS profiles. The energy deposition profiles were calculated with the simulations of 20 and 40 keV Ge implants into a B substrate. The vertical axis for the deposited energy was scaled so that the two deposited energy curves match the four B dose data points. The measured B dose data agree well with the scaled simulated energy deposition curves. This implies that the deposited energy distribution can be used to predict the knocked-in B dose. The predicted B doses reach maxima of about 3.6×10^{15} and $3.8 \times 10^{15} \text{ cm}^{-2}$ for B layer thicknesses of 10 and 17 nm with 20 and 40 keV Ge implants, respectively. It is desirable to maximize the recoil yield or the ratio of B dose to Ge dose for higher throughput. With the proper choice of the B layer thickness for a specific Ge energy between 20 and 40 keV, the recoil yield can be higher than 3.6 B atoms per Ge ion.

The sheet resistance should be roughly inversely proportional to the B dose despite deviations due to solid solubility limit, concentration-dependent mobility, and the defects re-

FIG. 6. Measured sheet resistance and the inverse of simulated energy deposition distribution as functions of thickness or depth of the B layer for 40 keV, 10^{15} cm^{-2} Ge implant and 950 or 1050 $^\circ\text{C}$ anneal for 10 s.

maining after the anneal. Hence, the sheet resistance is expected to be similar to a concave parabola function of B layer thickness in our experiments. Figure 6 shows the measured sheet resistance as a function of B layer thickness for 40 keV, 10^{15} cm^{-2} Ge implants and anneal temperatures of 950 and 1050 $^\circ\text{C}$. In Fig. 5, the simulations predicted that the B dose reaches a maximum at a B layer thickness of about 17 nm for 40 keV Ge implant. Meanwhile, the measured sheet resistance has a minimum at a B layer thickness of 15 nm (Fig. 6), which is in close agreement with the prediction. For comparison, the curve of the inverse of the deposited energy distribution is also shown in Fig. 6. The vertical scale of the inverse of the deposited energy is scaled so that the curve matches the measured sheet resistance data points for 1050 $^\circ\text{C}$ anneal.

Figure 7 shows the effect of the B layer thickness and Ge energy on the as-recoiled B profiles, with the Ge dose fixed at $1 \times 10^{15} \text{ cm}^{-2}$. The slopes of the B profiles are roughly the same regardless of the B layer thickness, while they are a strong function of Ge energy. Thus, the effect of the B layer thickness on the junction depth likely results

FIG. 7. As-recoiled B profiles for various thickness of B layers and 10^{15} cm^{-2} Ge implant at 20 or 40 keV.

FIG. 8. SIMS profiles of boron for 7.5, 15, and 25 nm thick deposited B layers, 20 keV, $1 \times 10^{15} \text{ cm}^{-2}$ Ge implant, and 950 °C anneal for 10 s.

from its effect on the B dose. The pronounced difference in the junction depth for the samples implanted with 20 keV Ge^+ mainly results from the difference in B dose.

The reproducibility of this process was also examined. Two samples were made at different times according to the same recipe of 15 nm B deposition and 40 keV, 10^{15} cm^{-2} Ge implant. The resultant B profiles were compared in Fig. 7. There is a 10% difference in junction depth at 10^{18} cm^{-3} and a 20% difference in B dose for these two samples. While the deviation can result from the variation in the B deposition step, the Ge implant, or the chemical etching step, it may also be caused by the SIMS measurements. For the SIMS measurements performed in this article, the error of the depth scale is expected to be within 5%–10%, and the error of the concentration can be expected to be in the 15%–20% range.²⁸

Figure 8 shows the effect of B layer thickness on the 950 °C-annealed B profiles, with the Ge implant recipe fixed at 20 keV, 10^{15} cm^{-2} . The thickest B layer (25 nm) results in the shallowest junction, though it also results in the highest sheet resistance (920 Ω/sq) and the lowest B dose among these three samples. The B profiles with 7.5 and 15 nm thick B layer deposition have a B hump, and the locations of the B humps are close to the predicted a/c interfaces respectively. On the other hand, the B profile with 25 nm B layer deposition does not have a B hump as the predicted a/c interface is very close to the surface.

In conclusion, the effects of the process parameters on the material properties of the junctions are summarized in Table I.

FIG. 9. Total B diffusion length at 10^{18} cm^{-3} for various B layer thicknesses and implantation Ge energies. The Ge dose is 10^{15} cm^{-2} . The anneal was performed at 950 °C for 10 s.

E. Alleviation of enhanced B diffusion

This junction fabrication process is likely to be less subject to transient enhanced diffusion (TED) of boron during the anneal. TED has been linked to the interaction between implantation-induced-damage and dopant diffusion.²⁴ In our process, the implant damage is concentrated in the boron layer and the surface region of Si. Following the implantation, the boron layer is chemically etched away, and the defects remaining in the Si are, thus, brought closer to the surface. Surface proximity of the defects has been proposed as an important factor for defect annihilation during the anneal.^{29–31} Therefore, TED may be alleviated in this recoil implantation method.

To investigate the effect of surface proximity on enhanced boron diffusion, total B diffusion lengths at 10^{18} cm^{-3} (i.e., the difference in junction depths at 10^{18} cm^{-3} between as-recoiled and annealed B profiles) as functions of B layer thickness for different Ge energies were examined, similar to the approach of Ref. 32. The Ge dose was fixed at 10^{15} cm^{-2} . The results are shown in Fig. 9. The total B diffusion length decreases as the thickness of the boron layer is increased and the Ge energy is reduced, which also make the EOR defects or the B humps closer to the surface. This implies the alleviation of enhanced B diffusion due to surface proximity of the defects.

F. Electrical properties

The electrical properties of the junctions formed by this recoil implantation technique were investigated. Test diodes were fabricated according to the 40 keV Ge implantation recipe mentioned in Sec. II. The SIMS boron profile of such a junction is shown in Fig. 4. The sheet resistance of such a

TABLE I. Summary of the effects of increasing each process parameter individually, with the rest of the process parameters fixed on the material properties of the junctions.

Process parameter (effect of increase)	Material properties	
	B profile	B dose
Ge energy	Becomes deeper	Also depends on B thickness
Ge dose	Slightly deeper	Increases
B film thickness	Also depends on Ge energy	Also depends on Ge energy

FIG. 10. I - V characteristic of a test diode fabricated with 15 nm thick deposited B layer, 40 keV, 10^{15} cm^{-2} Ge implant, and 950 °C anneal for 10 s.

doped layer is 240 Ω/sq , as measured with a four-point probe technique. The I - V characteristic of a $2 \times 10^5 \mu\text{m}^2$ diode is shown in Fig. 10. The leakage current density is 1.9 nA/cm² at -5 V bias. The forward ideality factor is about 1.07. This demonstrates good electrical properties of the junctions fabricated with our recoil implantation method.

IV. CONCLUSIONS

A novel recoil implantation technique has been developed for ultra-shallow junction formation. It has high throughput, and results in shallow B profiles and low sheet resistance. In addition, this process is efficient. The knock-in B dose can be higher than 3.6 times the Ge dose. Sub-60 nm deep junctions (measured at a reference dopant concentration of 10^{18} cm^{-3}) with sheet resistance lower than 1000 Ω/sq have been fabricated with this method (Figs. 4 and 8). The effects of the process parameters, such as B layer thickness, Ge energy, Ge dose, and anneal temperature, on the sheet resistance and recoil B profiles have been investigated. The repeatability and controllability of this process were also demonstrated. Simulations were performed to predict the as-implanted Ge and B profiles, and the experimental results agree well with the simulated results. Test diodes fabricated with this technique show good electrical characteristics with low leakage current.

A lower Ge energy results in a steeper as-recoiled B profile as well as alleviation of TED, while the B dose is not significantly reduced. Thus, with a lower Ge implantation energy such as 10 keV, it is possible to fabricate sub-40 nm deep p^+/n junctions with low sheet resistance, required for 0.1 μm CMOS transistors.

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