Charge-state changes of substitutional nitrogen impurities in silicon induced by additional impurities and defects

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Charge states of substitutional N impurities (N_s) in Si are found to be controllable by doping with P, B, and O impurities in N-ion implanted and subsequently pulsed-laser annealed Si (Si:N system). Electron-spin resonance measurements of the Si:N system doped with P, B, or O impurities show that the spin density of neutral N_s (N_s^0) decreases because of doping with these impurities. Compensation by multiple doping with equal amounts of P and B impurities leaves the density of N_s^0 essentially unchanged. These results yield evidence for charge-state changes of N_s due to the Fermi level shift. Oxygen doping is found to introduce donors. Three charge states, i.e., positive (N_s^+), neutral (N_s^0), and negative (N_s^-) are assigned to off-center substitutional N in Si.

I. INTRODUCTION

Nitrogen (N) impurities doped in Si are known to pin dislocations[1,2] in Si and suppress thermal oxidation[3,4] of Si. It was reported that N impurities retard silicide formation.[5] In addition, buried silicon-nitride layer formed by N-ion implantation is useful for an insulator and a diffusion barrier for impurities.[4,6,7] Therefore, N impurities in Si have been of technological interest in recent years.

There is, however, little information about substitutional or off-center substitutional N impurities (N_s) in Si, in contrast to the other group-V elements. This is attributed to the difficulty of introducing N_s into Si by the conventional doping techniques.[8] In fact, the equilibrium solid solubility of N in Si is low ($4.5 \pm 1.0 \times 10^{15}$ atoms/cm^3) (Ref. 9) as compared with that of the other donor- and acceptor-type impurities. On the other hand, it is known that N impurities are introduced into off-center substitutional sites of Si in excess of their solid solubility by means of N–ion implantation and subsequent pulsed-laser annealing (PLA).[10,11] This stimulated many kinds of experiments for N impurities in Si; e.g., deep-level transient spectroscopy (DLTS),[12,13] photoluminescence,[14–16] infrared absorption,[17,18] and electron spin resonance (ESR).[15,19–21] This also stimulated theoretical studies[22–24] of substitutional N impurities in Si. The electronic levels of N_s, however, have not as yet been clarified. Determination of the charge states of N_s is needed to understand electrical characteristics and diffusion kinetics for N in Si. This can be accomplished by the introduction of donor-type[19] or acceptor-type impurities into Si with N_s (Si:N system).

Moreover, the interactions between N and O impurities have been a growing interest. It was reported that N impurities enhance oxygen precipitation in Czochralski (CZ) Si wafers.[25] Stein[26] reported interactions of N pairs with O in pulsed-laser annealed Si and suggested that the interaction is controlled by O, which diffuses to sites near Si-N pairs. We found that O impurities have an effect on thermal annealing behavior of N_s.[21]

In this paper we report the effects of introducing P, B, and O impurities into the Si:N system and then discuss the charge states and electronic levels of N_s in Si. The impurity doping effects are investigated by the ESR measurements of various Si:N samples with additionally implanted impurities.

II. EXPERIMENTAL PROCEDURE

N ions (N_2^+) were implanted in CZ, B-doped (100) Si wafers with the resistivity of 30 ~ 50 Ω cm at an acceleration energy of 70 keV. P ions (P^+), B ions (B^+), and O ions (O_2^+) were subsequently implanted at acceleration energies of 70, 30, and 80 keV, respectively, to approximately overlap the profiles for N. The mean projected ranges (R_p) for 70 keV N_2^+, 70 keV P^+, 30 keV B^+, and 80 keV O_2^+ are about 940, 850, 970, and 940 Å, respectively.[27] The standard deviations for N_2, P, B, and O_2 ions are about 400, 340, 370, and 390 Å, respectively.[27] The ion implantation dose varied from 10^{12} to 10^{15}/cm^2 for P and B ion implantations and from 10^{12} to 10^{16}/cm^2 for O ion implantation. All the ion implantations were made at room temperature (RT) and in a vacuum lower than 4×10^{-6} Torr. The dose rates of the ion-implanted impurities were lower than 0.5 μA/cm^2.

All the ion implanted samples were annealed with a Q-switched ruby laser ($\lambda = 694$ nm, pulse duration = 40 ns) at energy densities from 1.2 to 1.5 J/cm^2. The anneal-beam irradiated samples in air through a quartz tube to homogenize a spatial variation in the beam intensity.

ESR measurements of these samples were made with a X-band (9-GHz) microwave incident upon TE_{011} cylindrical cavity at RT. For the measurement of conduction and/or donor electrons in P-doped Si:N samples, the ESR measurements were made at about 77 K. To avoid the saturation of ESR absorption of neutral N_s (N_s^0), the microwave power was made lower to 2 mW. The absolute number of N_s^0 in Si was determined relative to the known number of Mn^{2+} in MgO, as a spin standard. Thus, a variation in cavity Q does not affect our evaluation of the spin density of N_s^0. The absolute spin density was estimated to be uncertain by a factor less than 3, but the uncertainty in the relative density was less than ± 15%.

III. RESULTS AND DISCUSSION

A. Phosphorus and boron doping

Figure 1 shows ESR spectra of Si:N, P-doped Si:N (Si:N:P) and B-doped Si:N (Si:N:B) samples observed at RT. Three hyperfine (hf) lines of N_s^0 are clearly observed in the Si:N sample with 2×10^{14} N_2^+/cm^2, as shown in Fig. 1(a). It was reported by Brower[10] that the SL5 center assigned to N_s^0 has C_{3v} symmetry about $\langle 111 \rangle$ at temperatures below 100 K. This indicates that N is in off-center substitutional site rather than substitutional site of Si. Furthermore, we found from ESR measurements at RT that N_s^0 is isotropic (T_d symmetry) because of a motional effect.[11] In this case the g value and hf constant A are 2.0065 ± 0.0005 and 16.0 ± 0.3 G, respectively. It is found from Fig. 1 that these isotropic values are not changed by doping with P or B in the Si:N sample, but intensities for the hf lines of N_s^0 are decreased by P or B doping, as shown in Figs. 1(b) and 1(c). Possible effects of strong spin–spin interactions between localized spin of N_s^0 and degenerate P donor electrons must be considered when we interpret a decrease in N_s^0. However, since no significant change in ESR linewidth and g factor of N_s^0 was observed in the Si:N:P system, the decrease in N_s^0 cannot be explained by spin–spin interactions between N_s^0 and P donor electrons. The same result was obtained in dangling bonds of Si in degenerate Si:P systems.[28]

Figure 2 shows the effects of various doses of P and B impurities on N_s^0 in the Si:N samples with 2×10^{14} N_2^+/cm^2 and 5×10^{13} N_2^+/cm^2. The Ar impurity effect is also shown in Fig. 2 for comparison. Here, an acceleration energy of Ar ions (Ar^+) was 80 keV and R_p is about 770 Å. The spin density of N_s^0 decreases dramatically with P or B doses above certain critical doses. The critical doses of P and B for the Si:N sample with 2×10^{14} N_2^+/cm^2 are approximately $4\times10^{13} P^+/cm^2$ and 2×10^{13} B^+/cm^2, respectively. Average concentrations (dose/$2R_p$) of P and B for these critical doses are about $2\times10^{18}/cm^3$ and $1\times10^{18}/cm^3$, respectively. For the Si:N sample with 5×10^{13} N_2^+/cm^2, the critical doses of P and B are about 2×10^{13} P^+/cm^2 and 1×10^{13} B^+/cm^2, respectively. In contrast to P and B doping, N_s^0 remains constant for Ar doping to a dose of about 1×10^{15} Ar^+/cm^2. Results of Hall effect and Rutherford backscattering measurements[29] show that 100% of the P and B impurities (up to concentrations of $\sim5\times10^{21}/cm^3$ and $\sim1\times10^{21}/cm^3$, respectively) are electrically activated by PLA. It was also reported[29] that no macroscopic defects exist after PLA in Si doped with P and B up to these concentrations. In the present study the maximum concentration of P and B, corresponding to a dose of $1\times10^{15}/cm^2$, is about $1\times10^{20}/cm^3$. Consequently, ion-implanted P and B impurities are completely activated and the crystallinity of the Si:N system is not affected significantly by these P- or B-doping levels.

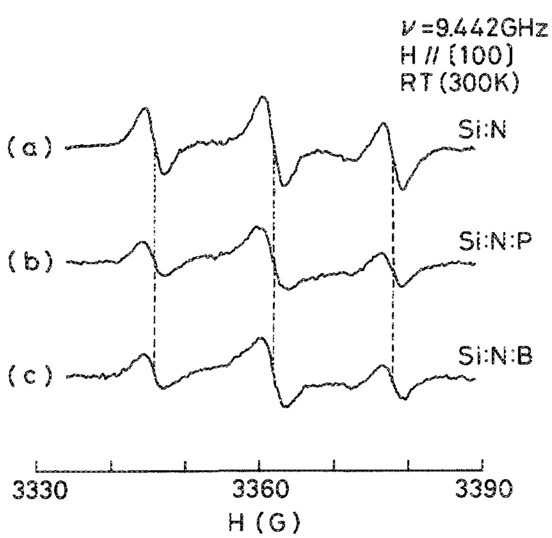

FIG. 1. (a) ESR spectrum of N_s^0 observed in the Si:N sample with a dose of 2×10^{14} N_2^+/cm^2. Doping effects of P and B on the N_s^0-ESR spectrum are shown in (b) and (c), respectively. Doses of P and B are 1×10^{14} P^+/cm^2 and 5×10^{13} B^+/cm^2, respectively. These spectra were observed at room temperature for H∥[100].

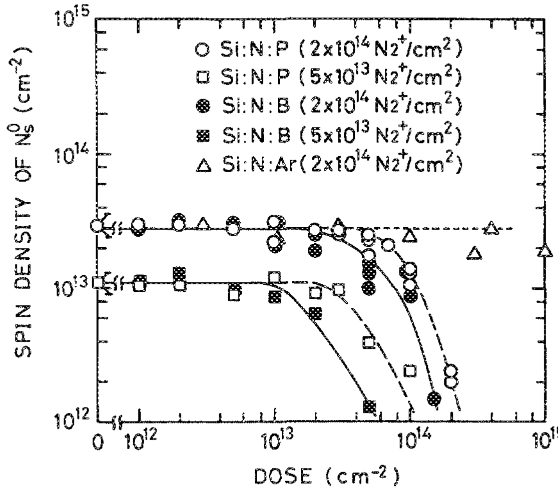

FIG. 2. P-, B-, and Ar-doping effects upon the neutral substitutional N impurity (N_s^0) density in the Si:N samples with N doses of 2×10^{14} N_2^+/cm^2 and 5×10^{13} N_2^+/cm^2. The abscissa indicates 70-keV-P^+, 30-keV-B^+, and 80-keV-Ar^+ dose levels.

The critical P dose necessary to decrease N_s^0 is found to be dependent upon the implanted N dose rather than the spin density. This was determined from measurements on a Si:N sample that had been implanted with 2×10^{15} N_2^+/cm^2. The spin density of N_s^0 for this higher dose was essentially the same as that for 2×10^{14} N_2^+/cm^2, but the critical P dose was about 7×10^{13} P^+/cm^2 compared to 4×10^{13} P^+/cm^2. Thus, the decrease in N_s^0 is caused by P doping rather than by direct interaction between N and P in Si.

The P-doping effect on the spin density of N_s^0 can be interpreted by change in charge states of N_s. In this case a negative charge state of N_s (N_s^-) is probably formed in the Si:N:P system. It was reported experimentally that N_s^0 is a deep-level donor and N-related paramagnetic defects exist in pulsed-laser annealed Si:N system.[10,11] Electronic levels for N_s^0, N_s^-, and other N-related (ΣN) defects are schematically illustrated in Fig. 3.[19] Without P doping, the Fermi level (E_F) is thought to be located between a level of N_s^0 and that

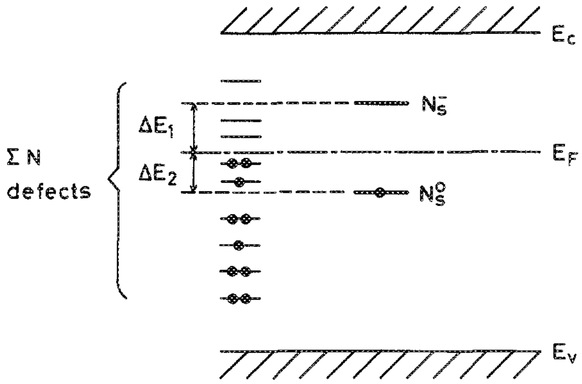

FIG. 3. Schematic energy diagram for N_s^0, N_s^-, and other N-related (ΣN) defects in Si:N. Levels with one or two electrons are in singly occupied or doubly occupied states, respectively.

of N_s^-. Doping with P donors will cause E_F to rise because P-donor electrons are trapped by levels of other ΣN defects, levels between the initial E_F and the level of N_s^- (ΔE_1 in Fig. 3). In the P-dose range below the critical dose, P-donor electrons are trapped only by levels of ΣN defects in ΔE_1 and the density of N_s^0 does not change. Above the critical P dose, E_F is shifted towards the level of the P, and so P donor electrons are trapped by N_s^0 to form diamagnetic N_s^- states in the Si:N:P system.[19]

To examine conduction and/or donor (C/D) electrons trapped by ΣN defects and N_s^0, ESR measurements of the Si:N:P samples were performed at about 77 K. ESR spectra observed are shown in Fig. 4. The spectrum of C/D electrons

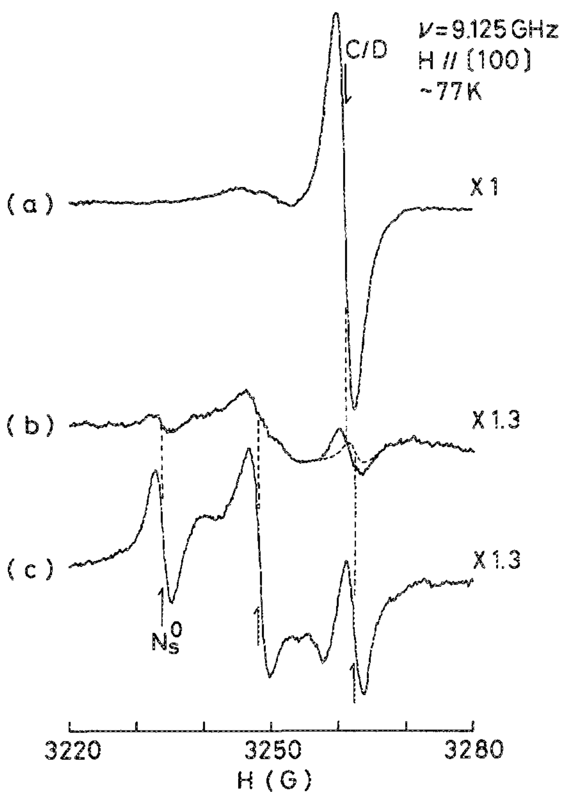

FIG. 4. ESR spectra of the Si:N:P samples with 1×10^{14} P^+/cm^2 observed at about 77 K for H‖[100]. N doses are (a) 5×10^{13} N_2^+/cm^2, (b) 2×10^{14} N_2^+/cm^2, and (c) 1×10^{15} N_2^+/cm^2. Both conduction and/or donor (C/D) electrons and N_s^0 are observed in (b).

($g=1.999$) is observed in the Si:N:P sample with 5×10^{13} N_2^+/cm^2 and 1×10^{14} P^+/cm^2 as shown in Fig. 4(a). It is found from Figs. 4(b) and 4(c) that C/D electrons decrease with increasing N dose. In the Si:N:P with 1×10^{15} N_2^+/cm^2 and 1×10^{14} P^+/cm^2, C/D electrons cannot be seen, while N_s^0 can be observed. Figure 5 shows N dose dependence of the spin density of C/D electrons and N_s^0 in the Si:N:P samples with 1×10^{14} P^+/cm^2 and 5×10^{13} P^+/cm^2. N dose dependence[11] of N_s^0 in the Si:N system is also represented by a dashed line in Fig. 5. The decrease in C/D electrons by doping with N indicates that ΣN defects with deep levels increase with N dose, and they trap C/D electrons. It should be also stressed that the number of the trap centers is approximately 50%–100% of that of the implanted N_2^+. This suggests that N pairs observed by Stein[17] in Si implanted with N may be dominant in ΣN. For N_2 dose $>10^{14}/cm^2$, N_s^0 becomes observable, while the C/D electrons almost disappear. The difference between the spin density of N_s^0 in the Si:N system and that in the Si:N:P system probably corresponds to a density of N_s^- in the Si:N:P system.

Similarly to the P doping, B doping decreases N_s^0 in the Si:N system, as shown in Fig. 2. This can also be explained by change in the charge states of N_s. In this case no shallow donors are added so that doping with B in the Si:N system causes E_F to fall. If the initial E_F is located just below the level of N_s^- within an energy difference of 0.06 eV, an increase in the spin density of N_s^0 should be observed at 300 K initially for B doping. However, the density of N_s^0 is not influenced within the experimental accuracy (15%) by the doping with B in the dose range below critical doses of about $10^{13}/cm^2$. This suggests that the initial E_F is not located just below the level of N_s^- but near the middle of the levels of N_s^0 and N_s^-. Thus, below the critical dose, B acceptors capture electrons from ΣN defects whose levels are located between the initial E_F and the level of N_s^0 (ΔE_2 in Fig. 3). In the B-dose range above the critical dose, E_F is shifted towards the

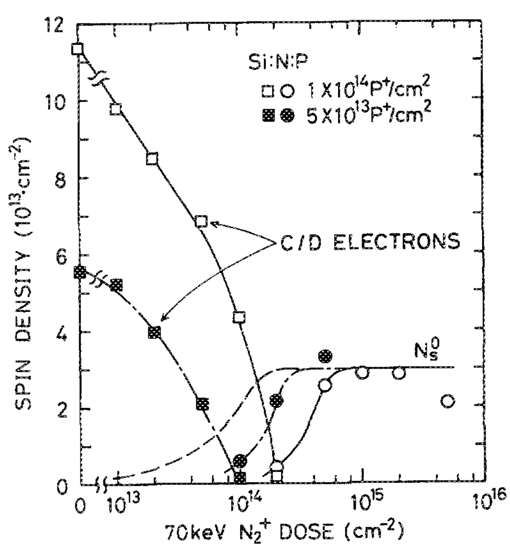

FIG. 5. Conduction and/or donor (C/D) electrons (squares) and N_s^0 (circles) in the Si:N:P samples with 1×10^{14} P^+/cm^2 (open) and 5×10^{13} P^+/cm^2 (closed), as functions of N_2^+ dose. N dose dependence of N_s^0 without P doping is shown by dashed line.

acceptor level of B, and then N_s with a positive charge (N_s^+) is possibly formed, which cannot be detected by ESR measurements. In contrast to this idea, one may consider that the decrease in N_s^0 by the B doping is due to pair formation of N_s and substitutional B impurities, and such a pair has no unpaired electron. This latter possibility must be ruled out because of the results of multiple doping with P and B in the Si:N system, as described later.

To confirm the idea of charge-state changes, multiple doping with P and B was carried out in the Si:N system. In this approach doping effects are independent of ΣN defects since electronic levels for B acceptors and P donors are most shallow. Figure 6 shows the results of multiple doping with P and B impurities in the Si:N system. The spin density of N_s^0 in the Si:N sample with 2×10^{14} N_2^+/cm^2 is about $3.8\times10^{13}/cm^2$ and decreases down to $1.9\times10^{13}/cm^2$ and $1\times10^{12}/cm^2$ with B doping at doses of 5×10^{13} B^+/cm^2 and 1.5×10^{14} B^+/cm^2, respectively (see Figs. 2 and 6). In the Si:N:B with 5×10^{13} B^+/cm^2, N_s^0 increases substantially when the P doping is around a dose of 5×10^{13} P^+/cm^2. A similar result is obtained for P doping in the Si:N:B with 1.5×10^{14} B^+/cm^2. These results illustrate the compensating effect between P donors and B acceptors and show that the decrease in N_s^0 by B or P doping is not caused by N_s-P or N_s-B pairing. We conclude, therefore, that the variation in N_s^0 observed in the Si:N:B and Si:N:P systems is due to changes in the charge states of the N_s.

B. Oxygen doping

The effect of doping with O impurities on N_s^0 in the Si:N system was examined to investigate interactions between N and O impurities (or O-related defect centers). Figure 7 shows the O-doping effect on N_s^0 for the Si:N samples with 2×10^{14} N_2^+/cm^2 and 5×10^{13} N_2^+/cm^2. The Ar-doping effect is also shown for comparison. For the Si:N:O sample, the spin density of N_s^0 changes anomalously in O dose range between 1×10^{14} O_2^+/cm^2 and 1×10^{15} O_2^+/cm^2, i.e., N_s^0 decreases with increasing O dose in the dose range from 1×10^{14} to 5×10^{14} O_2^+/cm^2 and increases in the range from 5×10^{14} to 1×10^{15} O_2^+/cm^2. No significant change in N_s^0 is seen below 1×10^{14} O_2^+/cm^2. In the dose range above 1×10^{15} O_2^+/cm^2, N_s^0 decreases with increasing O dose because of imperfect recrystallization like Ar implantation[30] above 1×10^{15} Ar^+/cm^2. The anomalous change in N_s^0 is not observed in Ar doping.

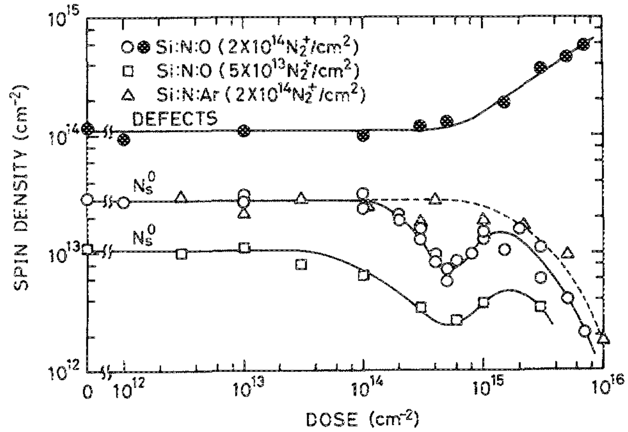

FIG. 7. O- and Ar-doping effects upon N_s^0 density in the Si:N samples with 2×10^{14} N_2^+/cm^2 and 5×10^{13} N_2^+/cm^2. The abscissa indicates 80-keV-O^{2+} and 80-keV-Ar^+ dose levels. The spin density of residual paramagnetic defects is also shown for the Si:N:O sample with 2×10^{14} N_2^+/cm^2 after pulsed-laser annealing.

He-ion implantation and multiple doping with O and B (or P) were performed to investigate the anomalous change in N_s^0 in the Si:N:O system. The results of He^+ implantation are shown in Fig. 8 for the Si:N:O sample with 2×10^{14} N_2^+/cm^2 and 5×10^{14} O_2^+/cm^2 in which the largest anomalous decrease is observed. N_s^0 in the Si:N:O system is increased by defect production with He-ion implantation, such as the case of the Si:N:P system. This suggests that new donor levels related with O impurities are formed in the Si:N:O system, and N_s^- states are generated.

Figure 9 shows B- and P-doping effects on N_s^0 for the Si:N:O samples with 3×10^{14} O_2^+/cm^2 and 5×10^{14}

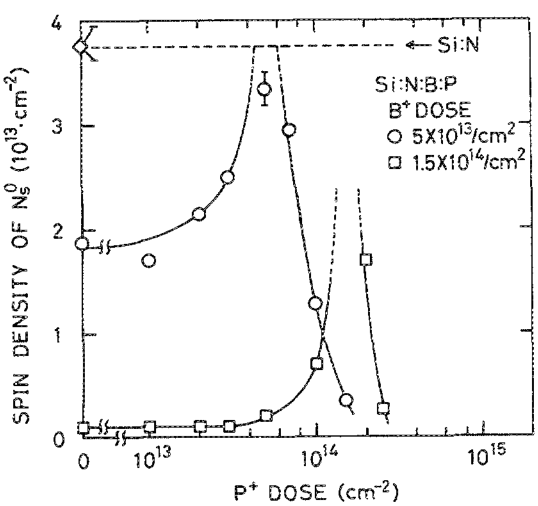

FIG. 6. P-doping effect on N_s^0 in the Si:N:B samples with 5×10^{13} B^+/cm^2 and 1.5×10^{14} B^+/cm^2. N dose in both samples is 2×10^{14} N_2^+/cm^2. Broken line indicates the spin density of N_s^0 in the Si:N with 2×10^{14} N_2^+/cm^2.

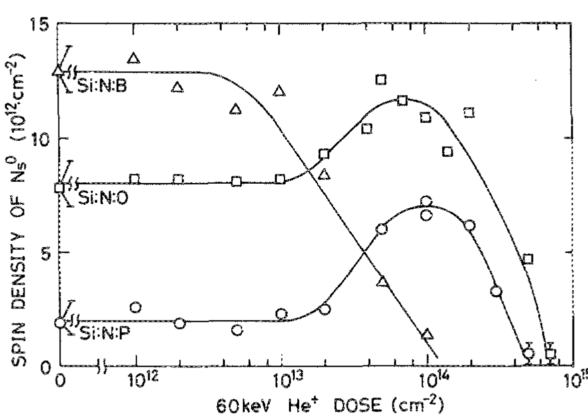

FIG. 8. He-ion implantation effect on N_s^0 in the Si:N:P sample with 2×10^{14} P^+/cm^2, the Si:N:B sample with 1×10^{14} B^+/cm^2 and the Si:N:O sample with 5×10^{14} O_2^+/cm^2. N dose in all samples is 2×10^{14} N_2^+/cm^2. The projected range of 60 keV He^+ is about 0.8 μm.

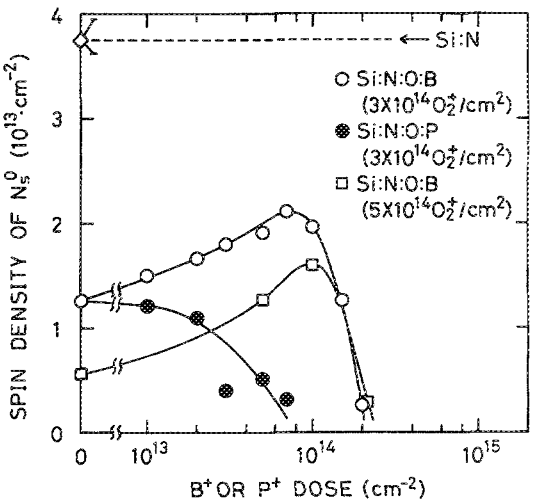

FIG. 9. B- and P-doping effects on N_s^0 in the Si:N:O samples with 3×10^{14} O_2^+/cm^2 and 5×10^{14} O_2^+/cm^2. N dose in both samples is 2×10^{14} N_2^+/cm^2. Broken line represents the initial density of N_s^0 in the Si:N.

O_2^+/cm^2. The spin density of N_s^0 in the Si:N:O system increases by B doping in the dose range up to 1.5×10^{14} B^+/cm^2. On the other hand, N_s^0 decreases by P doping. The quantitative change in N_s^0 due to B or P doping in the Si:N:O system suggests strongly that new O-related donors are formed and then N_s^0 changes to N_s^- by O doping in the Si:N. It leads to decrease in N_s^0. In regard to O-related donors, it was recently reported that a donor in CZ Si formed by PLA may be related with O impurities.[31] It is well known that thermal donors originate from O impurities.[32]

The increase in N_s^0 with O dose in the dose range from 5×10^{14} to 1×10^{15} O_2^+/cm^2 can be explained by significant production of other defects with levels deeper than that of N_s^-. Introduction of a high concentration of O impurities causes production of deep-level defects in Si. In fact, residual paramagnetic defects increase in O dose range above 5×10^{14} O_2^+/cm^2, as shown in Fig. 7. These defects trap an electron from N_s^- formed in the Si:N:O system and then N_s^- changes to N_s^0.

It is also found from Fig. 9 that N_s^0 in the Si:N:O samples with 3×10^{14} O_2^+/cm^2 and 5×10^{14} O_2^+/cm^2 recovers by B doping to about 60% and 40% of that in the Si:N sample, respectively. The anomalous decrease in N_s^0 is partly due to change in the charge states of N_s. The other part of decrement in N_s^0 is possibly caused by interactions between N_s and O impurities such as pairing of these impurities. In addition, the donor levels related with O impurities are thought to be formed most efficiently at a dose of 5×10^{14} O_2^+/cm^2 (see Fig. 7). The decrements of N_s^0 by O doping at 5×10^{14} O_2^+/cm^2 were $2\times10^{13}/cm^2$ and $8\times10^{12}/cm^2$ for the Si:N samples with 2×10^{14} N_2^+/cm^2 and 5×10^{13} N_2^+/cm^2, respectively. The decrement depends on N concentration in the Si:N:O system. This result suggests that a part of the decrement in N_s^0 is due to interactions between N_s and O.

C. Electronic energy levels

It is difficult to determine exactly the electronic levels for N_s in Si from the concentrations of P or B impurities in the Si:N system because some kinds of defects such as ΣN exist in the Si:N system. Approximate levels for N_s are estimated from the results of N dose dependence of C/D electrons and N_s^0 in the Si:N:P system and from DLTS measurements for the Si:N system. It should be stressed that, for example, ESR signals of both C/D electrons and N_s^0 can be observed in the Si:N:P sample with 2×10^{14} N_2^+/cm^2 and 1×10^{14} P^+/cm^2, as shown in Figs. 4(b) and 5. The spin density of P donor electrons and N_s^0 becomes about 2% of that in the Si:P sample only with 1×10^{14} P^+/cm^2 and about 10% of that in the Si:N sample only with 2×10^{14} N_2^+/cm^2, respectively. The latter shows that about 90% of N_s is in the state of N_s^-. These indicate that electrons occupy about 2% of P donor level and about 90% of N_s^- level at 77 K. Taking account of the Fermi–Dirac distribution function at 77 K, a difference in the energy levels between P donor and N_s^- is estimated to be about 40 meV. Since the maximum concentration of P is about $1\times10^{19}/cm^3$ in the Si:N:P sample with 1×10^{14} P^+/cm^2, the P donors form an impurity band in Si. However, it was assumed here that the width of the impurity band is narrow. Thus, the level of N_s^- is estimated to be about 80 meV under the bottom of the conduction band of Si (E_c-0.08 eV). Pantelides and Sah[33] reported that a calculated level of N_s^- is E_c-52.5 meV. Our estimated value is in reasonable agreement with the calculated value. To investigate deep levels in pulsed-laser annealed Si:N system, DLTS measurements of the Si:N system were performed. Three deep levels of E_c-0.31 eV, E_c-0.42 eV, and E_c-0.56 eV were observed. In particular, the level of E_c-0.31 eV increased with N dose in the Si:N system. It seems that the level of E_c-0.31 eV compares with a value (E_c-335.9 meV) for N_s^0 calculated by Pantelides and Sah.[33] More work is needed, however, for assignment of these observed levels. The DLTS and barrier-controlled ESR measurements are now in progress for the Si:N system to determine exact levels of N_s^- and N_s^0.

He-ion implantation of the Si:N:P and Si:N:B systems was performed to further check the approximate levels of N_s^0 and N_s^-. These are schematically illustrated in Fig. 10(a). Figure 8 shows the result of 60-keV–He^+ implantation in the Si:N:P with 2×10^{14} N_2^+/cm^2 and 2×10^{14} P^+/cm^2 and in the Si:N:B with 2×10^{14} N_2^+/cm^2 and 1×10^{14} B^+/cm^2. The initial spin densities of N_s^0 in the Si:N:P and Si:N:B samples decrease from $3.0\times10^{13}/cm^2$ to $2.0\times10^{12}/cm^2$ and $1.3\times10^{13}/cm^2$, respectively, because of the charge-state changes of N_s^0, as shown in Figs. 10(b) and 10(c) (see Sec. A). The He-ion implanted samples were not annealed in this case. The increase in N_s^0 in the Si:N:P sample is clearly observed with He-ion dose from 2×10^{13} He^+/cm^2 to 3×10^{14} He^+/cm^2, but is not observed in the Si:N:B sample. Our interpretation for the He^+ implantation effect is illustrated in Figs. 10(d) and 10(e) for the Si:N:P and Si:N:B systems, respectively. It was reported that He-ion implantation induces several deep-level defects (electron traps and hole traps) such as O-vacancy pairs and divacancy centers in Si,[34] similarly in the case for electron irradiation. Since the levels of induced defects are thought to be distributed in Si band gap, these levels cause gradually E_F to shift towards the middle of the band gap with increasing the He dose. Therefore,

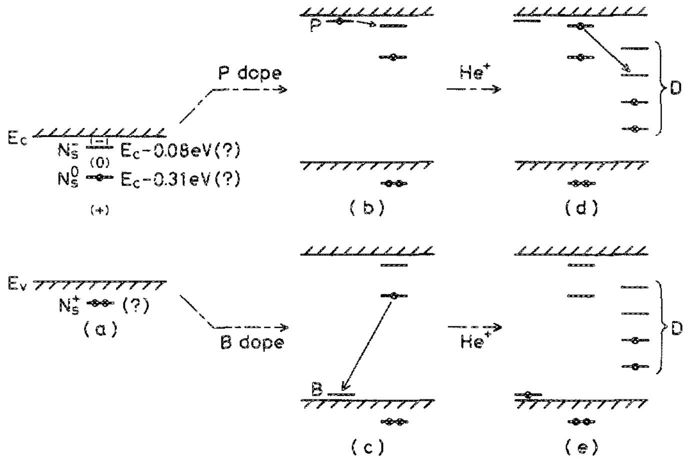

FIG. 10. (a) Schematic energy diagram of the substitutional N (N_s) in Si. Signs of +, 0, and − indicate charge states of N_s. A level of N_s^+ indicating a bonding state of Si-N is assumed to be under the top of the valence band. P- and B-doping effects on N_s are shown in (b) and (c), respectively. He^+ implantation effect is schematically illustrated in (d) and (e) for Si:N:P and Si:N:B systems, respectively. D represents levels of defects induced by He^+ implantation. Solid arrows represent an electron trapping.

the results of He-ion implantation can be interpreted by the Fermi level shift if the electronic levels of N_s (N_s^0 and N_s^- are located in the upper side of Si band gap.

IV. CONCLUSIONS

We have investigated the effects of doping with P (donor-type) and B (acceptor-type) impurities on substitutional N impurities (N_s) in the Si:N system in order to clarify electronic states of N_s in Si. The spin density of neutral substitutional N impurities (N_s^0) in the Si:N system decreases by introduction of P or B impurities. He-ion implantation causes increase in N_s^0 for Si:N:P system, while it causes decrease in N_s^0 for Si:N:B system. Multiple doping with equal amounts of P and B impurities shows no significant change in N_s^0, indicating their compensating effects. From these results, we conclude that substitutional N impurities (N_s) in Si exhibit at least three controllable charge states, i.e., neutral (N_s^0), negative (N_s^-), and positive (N_s^+) states. N_s^- and N_s^+ states are formed in the Si:N:P and Si:N:B systems, respectively, depending on the Fermi level position.

Furthermore, the effects of doping with O impurities on N_s^0 are first investigated. The spin density of N_s^0 decreases anomalously by O doping in the dose range between 1×10^{14} O_2^+/cm^2 and 1×10^{15} O_2^+/cm^2. Both He-ion implantation and B doping in the Si:N:O system cause increase in N_s^0, whereas P doping causes its decrease. The results yield evidence that new O-related donors are generated by pulsed-laser annealing, and then N_s^- states are formed in the Si:N:O system.

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[1]T. Abe, K. Kikuchi, S. Shirai, and S. Muraoka, in *Semiconductor Silicon 1981*, edited by H. R. Huff, R. J. Kriegler, and Y. Takeishi (Electrochemical Society, Pennington, NJ, 1981), p. 54.
[2]K. Sumino, I. Yonenaga, M. Imai, and T. Abe, J. Appl. Phys. **54**, 5016 (1983).
[3]W. J. M. J. Josquin and Y. Tamminga, J. Electrochem. Soc. **129**, 1803 (1982).
[4]W. J. M. J. Josquin, Nucl. Instrum. Methods **209/210**, 581 (1983).
[5]K. T. Ho, C.-D. Lien, and M-A. Nicolet, J. Appl. Phys. **57**, 232 (1985).
[6]R. J. Dexter, S. B. Watelski, and S. T. Picraux, Appl. Phys. Lett. **23**, 455 (1973).
[7]P. L. F. Hemment, R. F. Peart, M. F. Yao, K. G. Stephens, R. J. Chater, J. A. Kilner, D. Meekison, G. R. Booker, and R. P. Arrowsmith, Appl. Phys. Lett. **46**, 952 (1985).
[8]P. V. Pavlov, E. I. Zorin, D. I. Tetelbaum, and A. F. Khokhlov, Phys. Status Solidi A **35**, 11 (1976).
[9]Y. Yatsurugi, N. Akiyama, Y. Endo, and T. Nozaki, J. Electrochem. Soc. **120**, 975 (1973).
[10]K. L. Brower, Phys. Rev. B **26**, 6040 (1982).
[11]K. Murakami, K. Masuda, Y. Aoyagi, and S. Namba, Physica **116B**, 564 (1983).
[12]Y. Tokumaru, H. Okushi, T. Masui, and T. Abe, Jpn. J. Appl. Phys. **21**, L443 (1982).
[13]K. Nauka, M. S. Goorsky, H. C. Gatos, and J. Lagowski, Appl. Phys. Lett. **47**, 1341 (1985).
[14]H. C. Alt and L. Tapfer, in *Proceedings of the 13th International Conference on Defects in Semiconductors*, edited by L. C. Kimerling and J. M. Parsey, Jr. (The Metallurgical Society of American Institute of Mining, Metallurgical and Petroleum Engineers, Warrendale, PA, 1985), p. 833.
[15]K. Murakami, H. Itoh, K. Takita, K. Masuda, and T. Nishino, in *Proceedings of the 17th International Conference on Physics of Semiconductors*, edited by J. D. Chadi and W. A. Harrison (Springer, New York, 1985), p. 1493.
[16]A. Dörnen, G. Pensl, and R. Sauer, Phys. Rev. B **33**, 1495 (1986).
[17]H. J. Stein, in *Proceedings of the 13th International Conference on Defects in Semiconductors*, edited by L. C. Kimerling and J. M. Parsey, Jr. (The Metallurgical Society of American Institute of Mining, Metallurgical and Petroleum Engineers, Warrendale, PA, 1985), p. 839.
[18]H. J. Stein, Appl. Phys. Lett. **47**, 1339 (1985).
[19]K. Murakami, H. Itoh, K. Takita, and K. Masuda, Appl. Phys. Lett. **45**, 176 (1984).
[20]M. Sprenger, E. G. Sieverts, S. H. Muller, and C. A. J. Ammerlaan, Solid State Commun. **51** 951 (1984).
[21]H. Itoh, K. Murakami, K. Takita, and K. Masuda, in *Proceedings of the 14th International Conference on Defects in Semiconductors*, edited by H. J. von Bardeleben (Materials Science Forum, 1986), Vols. 10–12, p. 899.
[22]G. G. Deleo, W. B. Fowler, and G. D. Watkins, Phys. Rev. B **29** 3193 (1984).
[23]R. P. Messmer and P. A. Schultz, Solid State Commun. **52**, 563 (1984).
[24]H. P. Hjalmarson and D. R. Jennison, Phys. Rev. B **31**, 1208 (1985).
[25]F. Shimura and R. S. Hockett, Appl. Phys. Lett. **48**, 224 (1986).
[26]H. J. Stein, in *Proceedings of Materials Research Symposium on Microscopic Identification of Electronic Defects in Semiconductors*, edited by N. M. Johnson, S. G. Bishop, and G. D. Watkins (Materials Research Society, Pittsburgh, 1985), p. 287.
[27]D. K. Brice, in *Ion Implantation Range and Energy Deposition Distributions* (Plenum, New York, 1975).
[28]K. Murakami, K. Masuda, K. Gamo, and S. Namba, Appl. Phys. Lett. **30**, 300 (1977).
[29]M. Tamura, N. Natsuaki, and T. Tokuyama, in *Laser and Electron Beam*

Processing of Materials, edited by C. W. White and P. S. Peercy (Academic, New York, 1980), p. 247.

[30]A. G Cullis, H. C. Webber, J. M. Poate, and N. G. Chew, J. Microsc. **118**, 41 (1980).

[31]Y. Mada and N. Inoue, Appl. Phys. Lett. **48**, 1205, (1986).

[32]See, for example, G. S. Oehrlein and J. W. Corbett, in *Proceedings of Materials Research Society Symposium on Defects in Semiconductors II*, edited by S. Mahajan and J. W. Corbett (Elsevier, New York, 1983), p. 107.

[33]S. T. Pantelides and C. T. Sah, Phys. Rev. B **10**, 638 (1974).

[34]K. L. Wang, J. Appl. Phys. **53**, 449 (1982).