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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⁺) 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⁺ (N⁺) decreases because of doping with these impurities. Compensation by multiple doping with equal amounts of P and B impurities leaves the density of N⁺ essentially unchanged. These results yield evidence for charge-state changes of N⁺ due to the Fermi level shift. Oxygen doping is found to introduce donors. Three charge states, i.e., positive (N⁺), neutral (N⁰), and negative (N⁻) are assigned to off-center substitutional N in Si.

I. INTRODUCTION

Nitrogen (N) impurities doped in Si are known to pin dislocations in Si and suppress thermal oxidation of Si. It was reported that N impurities retard silicide formation. In addition, buried silicon-nitride layer formed by N-ion implantation is useful for an insulator and a diffusion barrier for impurities. 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⁺) in Si, in contrast to the other group-V elements. This is attributed to the difficulty of introducing N⁺ into Si by the conventional doping techniques. In fact, the equilibrium solid solubility of N in Si is low (4.5 ± 1.0 × 10¹⁸ atoms/cm³) (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). This stimulated many kinds of experiments for N impurities in Si; e.g., deep-level transient spectroscopy (DLTS), photoluminescence, infrared absorption, and electron spin resonance (ESR). This also stimulated theoretical studies of N impurities in Si. The electronic levels of N⁺, however, have not as yet been clarified. Determination of the charge states of N⁺ is needed to understand electrical characteristics and diffusion kinetics for N in Si. This can be accomplished by the introduction of donor-type or acceptor-type impurities into Si with N⁺ (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. 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⁺.

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⁺ 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⁺) 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⁺) were subsequently implanted at acceleration energies of 70, 30, and 80 keV, respectively, to approximately overlap the profiles for N. The mean projected ranges (Rₚ) for 70 keV N⁺, 70 keV P⁺, 30 keV B⁺, and 80 keV O⁺ are about 940, 850, 970, and 940 Å, respectively. The standard deviations for N, P, B, and O ions are about 400, 340, 370, and 390 Å, respectively. The ion implantation dose varied from 10¹⁰ to 10¹⁵/cm² for P and B ion implantations and from 10¹⁰ to 10¹⁵/cm² 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/cm².

All the ion implanted samples were annealed with a Q-switched ruby laser (λ = 694 nm, pulse duration = 40 ns) at energy densities from 1.2 to 1.5 J/cm². 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 TE₀₁₁ 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⁺ (N⁰), the microwave power was made lower to 2 mW. The absolute number of N⁰ in Si was determined relative to the known number of Mn²⁺ in MgO, as a spin standard. Thus, a variation in cavity Q does not affect our evaluation of the spin density of N⁰. 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%.

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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$_{0}^{+}$ are clearly observed in the Si:N sample with $2 \times 10^{14}$ N$_{2}^{+}$/cm$^{2}$, as shown in Fig. 1(a). It was reported by Brower$^{10}$ that the SL5 center assigned to N$_{0}^{+}$ has C$_{3v}$ symmetry about (111) 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$_{0}^{+}$ 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$_{0}^{+}$ 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$_{0}^{+}$ and degenerate P donor electrons must be considered when we interpret a decrease in N$_{0}^{+}$. However, since no significant change in ESR linewidth and g factor of N$_{0}^{+}$ was observed in the Si:N:P system, the decrease in N$_{0}^{+}$ cannot be explained by spin–spin interactions between N$_{0}^{+}$ 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$_{0}^{+}$ in the Si:N samples with $2 \times 10^{14}$ N$_{2}^{+}$/cm$^{2}$ and $5 \times 10^{13}$ 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$_{0}^{+}$ decreases dramatically with P or B doses above certain critical doses. The critical doses of P and B for the Si:N sample with $2 \times 10^{14}$ N$_{2}^{+}$/cm$^{2}$ are approximately $4 \times 10^{13}$P$^{+}$/cm$^{2}$ and $2 \times 10^{13}$ B$^{+}$/cm$^{2}$, respectively. Average concentrations (dose/2$R_{p}$) of P and B for these critical doses are about $2 \times 10^{18}$/cm$^{2}$ and $1 \times 10^{19}$/cm$^{3}$, respectively. For the Si:N sample with $5 \times 10^{13}$ N$_{2}^{+}$/cm$^{2}$, the critical doses of P and B are about $2 \times 10^{13}$ P$^{+}$/cm$^{2}$ and $1 \times 10^{13}$ B$^{+}$/cm$^{2}$, respectively. In contrast to P and B doping, N$_{0}^{+}$ remains constant for Ar doping to a dose of about $1 \times 10^{15}$ 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 $5 \times 10^{21}$/cm$^{3}$ and $1 \times 10^{23}$/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 $1 \times 10^{15}$/cm$^{2}$, is about $1 \times 10^{20}$/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.

The critical P dose necessary to decrease N$_{0}^{+}$ 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 $2 \times 10^{15}$ N$_{2}^{+}$/cm$^{2}$. The spin density of N$_{0}^{+}$ for this higher dose was essentially the same as that for $2 \times 10^{14}$ N$_{2}^{+}$/cm$^{2}$, but the critical P dose was about $7 \times 10^{13}$ P$^{+}$/cm$^{2}$ compared to $4 \times 10^{13}$ P$^{+}$/cm$^{2}$. Thus, the decrease in N$_{0}^{+}$ 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$_{0}^{+}$ can be interpreted by change in charge states of N$_{0}^{+}$. In this case a negative charge state of N$_{0}^{−}$ (N$_{0}^{−}$) is probably formed in the Si:N:P system. It was reported experimentally that N$_{0}^{−}$ is a deep-level donor and N-related paramagnetic defects exist in pulsed-laser annealed Si:N system.$^{10,11}$ Electronic levels for N$_{0}^{−}$, N$_{2}^{+}$, and other N-related ($\Sigma$N) defects are schematically illustrated in Fig. 3. Without P doping, the Fermi level ($E_{F}$) is thought to be located between a level of N$_{0}^{−}$ and that
of N$_p^-$. Doping with P donors will cause $E_F$ to rise because P-donor electrons are trapped by levels of other $\Sigma N$ defects, levels between the initial $E_F$ and the level of N$_p^-$ ($\Delta E_1$ in Fig. 3). In the P-dose range below the critical dose, P-donor electrons are trapped only by levels of $\Sigma N$ defects in $\Delta E_1$ and the density of N$_p^0$ 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$_p^0$ to form diamagnetic N$_p^-$ states in the Si:N:P system.$^{19}$

To examine conduction and/or donor (C/D) electrons trapped by $\Sigma N$ defects and N$_p^0$, 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

$$ (g = 1.999) $$ is observed in the Si:N:P sample with $5 \times 10^{13}$ N$_p^2$ /cm$^2$ and $1 \times 10^{14}$ 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 $1 \times 10^{15}$ N$_p^+$/cm$^2$ and $1 \times 10^{14}$ P$^+$/cm$^2$, C/D electrons cannot be seen, while N$_p^0$ can be observed. Figure 5 shows N dose dependence of the spin density of C/D electrons and N$_p^0$ in the Si:N:P samples with $1 \times 10^{14}$ P$^+$/cm$^2$ and $5 \times 10^{13}$ P$^+$/cm$^2$. N dose dependence of N$_p^0$ 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 $\Sigma N$ 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$_p^-$. This suggests that N pairs observed by Stein$^{17}$ in Si implanted with N may be dominant in $\Sigma N$. For N$_p$ dose $> 1 \times 10^{14}$/cm$^2$, N$_p^0$ becomes observable, while the C/D electrons almost disappear. The difference between the spin density of N$_p^0$ in the Si:N system and that in the Si:N:P system corresponds to a density of N$_p^-$ in the Si:N:P system.

Similarly to the P doping, B doping decreases N$_p^0$ in the Si:N system, as shown in Fig. 2. This can also be explained by change in the charge states of N$_p^-$. 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$_p^-$ within an energy difference of 0.06 eV, an increase in the spin density of N$_p^0$ should be observed at 300 K initially for B doping. However, the density of N$_p^0$ 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$_p^-$ but near the middle of the levels of N$_p^0$ and N$_p^-$. Thus, below the critical dose, B acceptors capture electrons from $\Sigma N$ defects whose levels are located between the initial $E_F$ and the level of N$_p^0$ ($\Delta E_2$ in Fig. 3). In the B-dose range above the critical dose, $E_F$ is shifted towards the
acceptor level of B, and then N\textsubscript{A} with a positive charge (N\textsubscript{A}\textsuperscript{+}) is possibly formed, which cannot be detected by ESR measurements. In contrast to this idea, one may consider that the decrease in N\textsubscript{O} by B doping is due to pair formation of N\textsubscript{A} 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 Si:N 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\textsubscript{O} in the Si:N sample with 2\times10\textsuperscript{14} N\textsubscript{A}\textsuperscript{+}/cm\textsuperscript{2} is about 3.8\times10\textsuperscript{13}/cm\textsuperscript{2} and decreases down to 1.9\times10\textsuperscript{13}/cm\textsuperscript{2} and 1\times10\textsuperscript{12}/cm\textsuperscript{2} with B doping at doses of 5\times10\textsuperscript{13} B\textsuperscript{+}/cm\textsuperscript{2} and 1.5\times10\textsuperscript{14} B\textsuperscript{+}/cm\textsuperscript{2}, respectively [see Figs. 2 and 6]. In the Si:N:B with 5\times10\textsuperscript{13} B\textsuperscript{+}/cm\textsuperscript{2}, N\textsubscript{O} increases substantially when the P doping is around a dose of 5\times10\textsuperscript{13} P\textsuperscript{+}/cm\textsuperscript{2}. A similar result is obtained for P doping in the Si:N:B with 1.5\times10\textsuperscript{14} B\textsuperscript{+}/cm\textsuperscript{2}. These results illustrate the compensating effect between P donors and B acceptors and show that the decrease in N\textsubscript{O} by B or P doping is not caused by N\textsubscript{A}-P or N\textsubscript{A}-B pairing. We conclude, therefore, that the variation in N\textsubscript{O} observed in the Si:N:B and Si:N:P systems is due to changes in the charge states of the N\textsubscript{A}.

B. Oxygen doping

The effect of doping with O impurities on N\textsubscript{O} 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\textsubscript{O} for the Si:N samples with 2\times10\textsuperscript{14} N\textsubscript{A}\textsuperscript{+}/cm\textsuperscript{2} and 5\times10\textsuperscript{13} N\textsubscript{A}\textsuperscript{+}/cm\textsuperscript{2}. The Ar-doping effect is also shown for comparison. For the Si:N:B sample, the spin density of N\textsubscript{O} changes anomalously in O dose range between 1\times10\textsuperscript{14} O\textsubscript{2}\textsuperscript{+}/cm\textsuperscript{2} and 1\times10\textsuperscript{15} O\textsubscript{2}\textsuperscript{+}/cm\textsuperscript{2}, i.e., N\textsubscript{O} decreases with increasing O dose in the dose range from 1\times10\textsuperscript{14} to 5\times10\textsuperscript{14} O\textsubscript{2}\textsuperscript{+}/cm\textsuperscript{2} and increases in the range from 5\times10\textsuperscript{14} to 1\times10\textsuperscript{15} O\textsubscript{2}\textsuperscript{+}/cm\textsuperscript{2}. No significant change in N\textsubscript{O} is seen below 1\times10\textsuperscript{14} O\textsubscript{2}\textsuperscript{+}/cm\textsuperscript{2}. In the dose range above 1\times10\textsuperscript{15} O\textsubscript{2}\textsuperscript{+}/cm\textsuperscript{2}, N\textsubscript{O} decreases with increasing O dose because of imperfect recrystallization like Ar implantation above 1\times10\textsuperscript{15} Ar\textsuperscript{+}/cm\textsuperscript{2}. The anomalous change in N\textsubscript{O} is not observed in Ar doping.

He-ion implantation and multiple doping with O and B (or P) were performed to investigate the anomalous change in N\textsubscript{O} in the Si:N:O system. The results of He\textsuperscript{+} implantation are shown in Fig. 8 for the Si:N:O sample with 2\times10\textsuperscript{14} N\textsubscript{A}\textsuperscript{+}/cm\textsuperscript{2} and 5\times10\textsuperscript{14} O\textsubscript{2}\textsuperscript{+}/cm\textsuperscript{2} in which the largest anomalous decrease is observed. N\textsubscript{O} 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\textsubscript{O} states are generated.

Figure 9 shows B- and P-doping effects on N\textsubscript{O} for the Si:N:O samples with 3\times10\textsuperscript{14} O\textsubscript{2}\textsuperscript{+}/cm\textsuperscript{2} and 5\times10\textsuperscript{14} O\textsubscript{2}\textsuperscript{+}/cm\textsuperscript{2}.

![Image of Figure 6](http://example.com/image6.png)

**FIG. 6.** P-doping effect on N\textsubscript{O} in the Si:N:B samples with 5\times10\textsuperscript{13} B\textsuperscript{+}/cm\textsuperscript{2} and 1.5\times10\textsuperscript{14} B\textsuperscript{+}/cm\textsuperscript{2}. N\textsubscript{O} dose in both samples is 2\times10\textsuperscript{14} N\textsubscript{A}\textsuperscript{+}/cm\textsuperscript{2}. Broken line indicates the spin density of N\textsubscript{O} in the Si:N with 2\times10\textsuperscript{14} N\textsubscript{A}\textsuperscript{+}/cm\textsuperscript{2}.

![Image of Figure 7](http://example.com/image7.png)

**FIG. 7.** O and Ar-doping effects upon N\textsubscript{O} density in the Si:N samples with 2\times10\textsuperscript{14} N\textsubscript{A}\textsuperscript{+}/cm\textsuperscript{2} and 5\times10\textsuperscript{13} N\textsubscript{A}\textsuperscript{+}/cm\textsuperscript{2}. The abscissa indicates 80-keV O\textsuperscript{2}\textsuperscript{+} and 80-keV Ar\textsuperscript{+} dose levels. The spin density of residual paramagnetic defects is also shown for the Si:N:O sample with 2\times10\textsuperscript{14} N\textsubscript{A}\textsuperscript{+}/cm\textsuperscript{2} after pulsed-laser annealing.

![Image of Figure 8](http://example.com/image8.png)

**FIG. 8.** He-ion implantation effect on N\textsubscript{O} in the Si:N:P sample with 2\times10\textsuperscript{14} P\textsuperscript{+}/cm\textsuperscript{2}, the Si:N:B sample with 1\times10\textsuperscript{14} B\textsuperscript{+}/cm\textsuperscript{2} and the Si:N:O sample with 5\times10\textsuperscript{14} O\textsubscript{2}\textsuperscript{+}/cm\textsuperscript{2}. N\textsubscript{O} dose in all samples is 2\times10\textsuperscript{14} N\textsubscript{A}\textsuperscript{+}/cm\textsuperscript{2}. The projected range of 60 keV He\textsuperscript{+} is about 0.8 \mu m.
the Si:N system because some kinds of defects such as \( \Sigma \)N exist in the Si:N system. Approximate levels for \( N_0 \) are estimated from the results of N dose dependence of C/D electrons and \( N_0^+ \) 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 \( N_0^+ \) can be observed in the Si:N:P sample with \( 2 \times 10^{14} \) \( N_0^+ \)/cm\(^2\) and \( 1 \times 10^{14} \) P\(^+\)/cm\(^2\), as shown in Figs. 4(b) and 5. The spin density of P donor electrons and \( N_0^+ \) becomes about 2% of that in the Si:P sample only with \( 1 \times 10^{14} \) P\(^+\)/cm\(^2\) and about 10% of that in the Si:N sample only with \( 2 \times 10^{14} \) N\(^+_0\)/cm\(^2\), respectively. The latter shows that about 90% of \( N_0 \) is in the state of N\(^-_0\). These indicate that electrons occupy about 2% of P donor level and about 90% of N\(^-_0\) 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\(^-_0\) is estimated to be about 40 meV. Since the maximum concentration of P is about \( 1 \times 10^{15}/\text{cm}^2\) in the Si:N:P sample with \( 1 \times 10^{14} \) 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\(^-_0\) 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\(^-_0\) 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 \( N_0^+ \) 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\(^-_0\) and N\(^0\).

He-ion implantation of the Si:N:P and Si:N:B systems was performed to further check the approximate levels of \( N_0^+ \) and N\(^-_0\). These are schematically illustrated in Fig. 10(a). Figure 8 shows the result of 60-keV He\(^+\) implantation in the Si:N:P with \( 2 \times 10^{14} \) \( N_0^+ \)/cm\(^2\) and \( 2 \times 10^{14} \) P\(^+\)/cm\(^2\) and in the Si:N:B with \( 2 \times 10^{14} \) N\(^+_0\)/cm\(^2\) and \( 1 \times 10^{14} \) B\(^+\)/cm\(^2\). The initial spin densities of \( N_0^+ \) in the Si:N:P and Si:N:B samples decrease from \( 3.0 \times 10^{13}/\text{cm}^2\) to \( 2.0 \times 10^{13}/\text{cm}^2\) and \( 1.3 \times 10^{13}/\text{cm}^2\), respectively, because of the charge-state changes of \( N_0^+ \), 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 \( N_0^+ \) in the Si:N:P sample is clearly observed with He-ion dose from \( 2 \times 10^{13} \) He\(^+\)/cm\(^2\) to \( 3 \times 10^{14} \) 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 \( E_c \) to shift towards the middle of the band gap with increasing the He dose. Therefore,
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FIG. 10. (a) Schematic energy diagram of the substitutional N (N_s) in Si. Signs of +, 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^0) 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+ 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 $1 \times 10^{14}$ O^2+ /cm$^2$ and $1 \times 10^{15}$ O^2+ /cm$^2$. Both He+ 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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