Electron-Beam Doping (Wada's Experiments*)

—New phenomena and New Technology — I. Experiments (Review)

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3−9MeV electrons were used to introduce impurity In (Ga, Sb, Ge, W) atoms into Ge(Si) wafers from In(GaSb, Sb, Ge, W) sheets, which were in contact with a Ge(Si) surfase. Three kinds of concentration-dependent diffusivities ($\sim 10^{-20}-10^{-12}cm^2\ sec^{-1}$) for volume diffusions and the largest diffusivities such as $10^{-8}-10^{-6}cm^2\ sec^{-1}$ for a surface diffusion were measured. Activation energies of sputtering yield for Ge and of the diffusivity of Ge in Si were estimated to be ~0.44 eV and ~0.85 eV, respectively. Dependences of impurity concentration on Ge sheet thickness, on electron energy and on electron fluence were investigated.

U-shaped diffusion profiles of the impurities in the substrate were experimentally obtained. These results may be explained well by considering both the equilibrium condition [substitutional impurity + self-interstitial ⇄ interstitial impurity (the "kick-out" mechanism)] and the surface diffusion process.

1. Introduction

The physical properties of semiconductors irradiated by high energy electrons have been studied by many workers.[1-34)]

Ion implantation has been developed into a successful technique for doping semiconductor materials. It is well known that ion implantation in semiconductors is accompanied by severe radiation damage introduced with the implantation process.[35)] In silicon, with low ion doses, the damage takes the form of amorphous zones,[36)] and when irradiation is continued, the zones overlap to form a continuous amorphous layer.

The important basis for the use of electrons lies in the fact that as long as the energy of the electrons is close to the displacement threshold, it is presumed that only single Frenkel pairs are formed. Electron irradiation avoids the complication attendant upon the generation of complex damage region presumed to occur in neutron and heavy-charged particle irradiation.

A new method of electron beam doping was reported by one of the authors Wada.[37,38)] The technique employs an impurity sheet in contact with the semiconductor surface which is bombarded with high energy electrons.[39-45)]

In the present paper the introductions of Ge, Sb and W impurities into Si at temperatures of 20−60℃, ~170℃ and ~360℃ are investigated. The diffusivity of Ge impurity in Si, an activation energy of sputtering yield for Ge and an activation energy of the diffusivity of Ge are estimated. Dependences of impurity concentrations on Ge sheet thickness and on electron energy are observed. U-shaped diffusion profiles in semiconductors by high-energy electron-beam doping[37-45)] are investigated. In the experiments, a large buildup of impurity concentration at both front and back surfaces of the substrate, and unusual, much larger diffusivities of impurity atoms during electron bombardment at room temperature are observed. These behaviors may be explained well by taking account of the surface diffusion and the kick-out mechanism.

2. Experimental procedure

The samples used in the experiments are

* One of the authors (Wada) presented the invited paper[38)] at the 3rd international conference on neutron transmutation doped silicon in Copenhagen, August, 1980. In that time, Dr. Jens Guldberg of the conference chairman introduced in the conference opening address that Wada's experiments were remarkable as a new type of impurity doping method.

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Table 1. Impurity sheets and substrates used in the experiments.

	Material	purity, conduction type resistivity orientation, thickness
Impurity sheet	In	99.999%, t=0.3 mm
	GaSb	p type (undoped), ρ=0.0545 Ωcm ⟨100⟩, t=0.5 mm
	W	99.99%, t=0.1 mm
	Ge	n type (Sb doped), ρ=2.5 Ωcm ⟨111⟩, t=0.26 mm
	Sb	99.9999%, t=0.33 mm
Substrate	Ge	n type (undoped), ρ>30 Ωcm ⟨111⟩, t=0.67-0.74 mm
		p type (In doped), ρ=2-3 Ωcm ⟨111⟩, t=0.67-0.84 mm
	Si	n type (P doped), ρ=3-6 Ωcm ⟨100⟩, t=0.36 mm

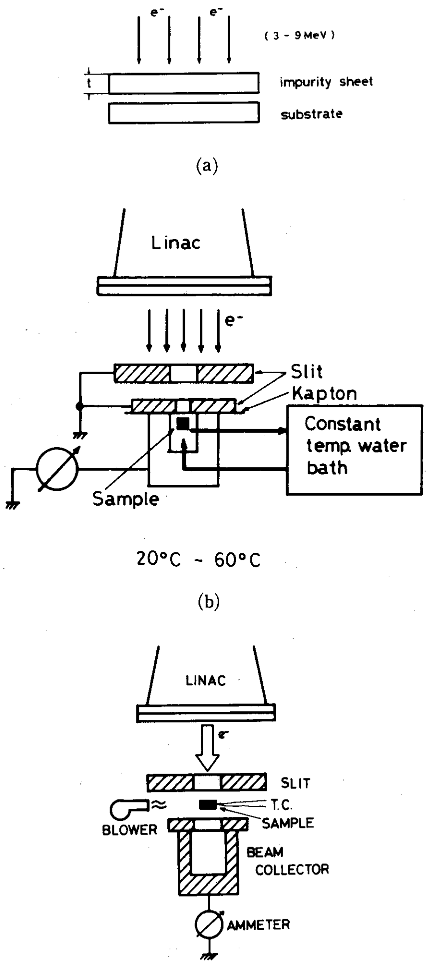


Fig. 1 (a) Schematic diagram of electron beam doping.
(b) Schematic diagram of electron bombardment at 20−60℃ and (c) at 170−360℃.

summarized in Table 1. t represents the thickness of impurity sheets or substrates. The surfaces of the impurity sheets in contact with the Ge(Si) wafer were bombarded with a total fluence of about $(1-5)\times10^{17}$ electrons cm^{-2} at 7MeV from an electron linear accelerator [Fig. 1(a)], with a pulse width of ~3.5 μsec, a 200 Hz duty cycle, and an average electron-beam current of 20 μA.

In the case of 20−60℃ irradiation, the samples were put in a circulating water bath, which was kept at a constant temperature by using a thermoregulator, as shown in Fig. 1(b). In hot (170℃ and 360℃) irradiation, the samples were air-cooled by a blower, as shown in Fig. 1(c). The introductions of impurity atoms in Si were measured using both Rutherford backscattering spectroscopy (RBS) and secondary ion mass spectroscopy (SIMS). The majority-carrier sign was determined by a hot-probe type.

In the experiment of Ge/Si, the depth distributions of relative intensity of impurity atoms in the SIMS measurements were in good agreement with the results obtained by Rutherford backscattering[40](RBS).

3. Experimental results

A. Typical

Fig. 2 shows the backscattering spctrum in the random and aligned conditions by 1.8 MeV He^+ ions in the case of Sb (t~0.33mm)/Si irradiated at ~170℃ with a total fluence of $\sim5\times10^{17}$ electrons cm^{-2} at 7 MeV. The figure indicates the introduction of Sb impurities into Si in a depth range of $x<\sim1.1\mu m$ and the maximum Sb concentration of $\sim7\times10^{20}cm^{-3}$ at the Si surface. After the hot (~170℃) irradiation, the conductivity type at the front surface of the substrates varid to n-type (Table 2). For p-Si wafers bombarded with a

Table 2. Conductivity type after electron beam doping.

	Sample I	Sample II
7 MeV 5×10^{17} e/cm² 170°C	e⁻ e⁻ p-Si	e⁻ e⁻ Sb 0.33mm p-Si
Conductivity type	p-type	n-type (conversion)

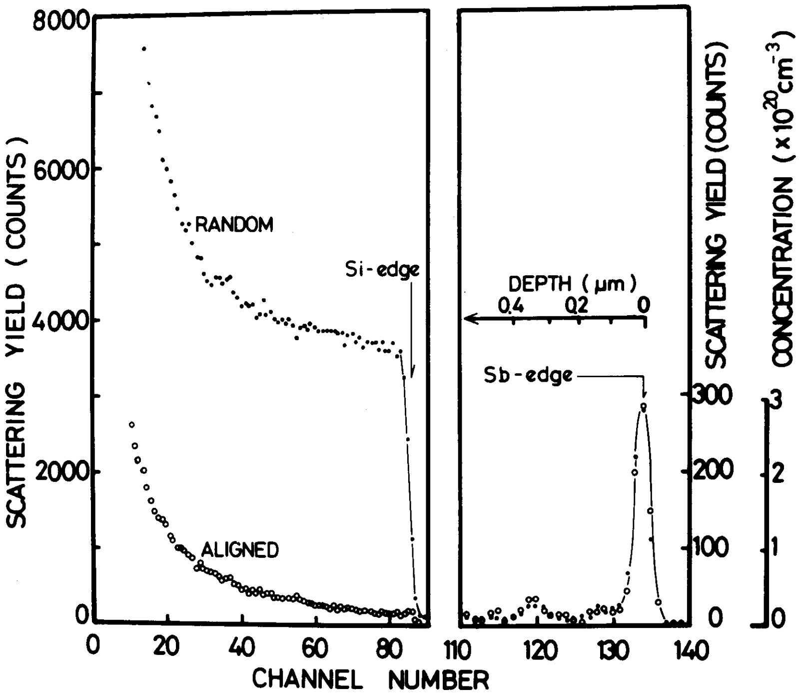


Fig. 2　Backscattering spectra for the case of Sb overlayers and Si substrates in the random and aligned conditions.

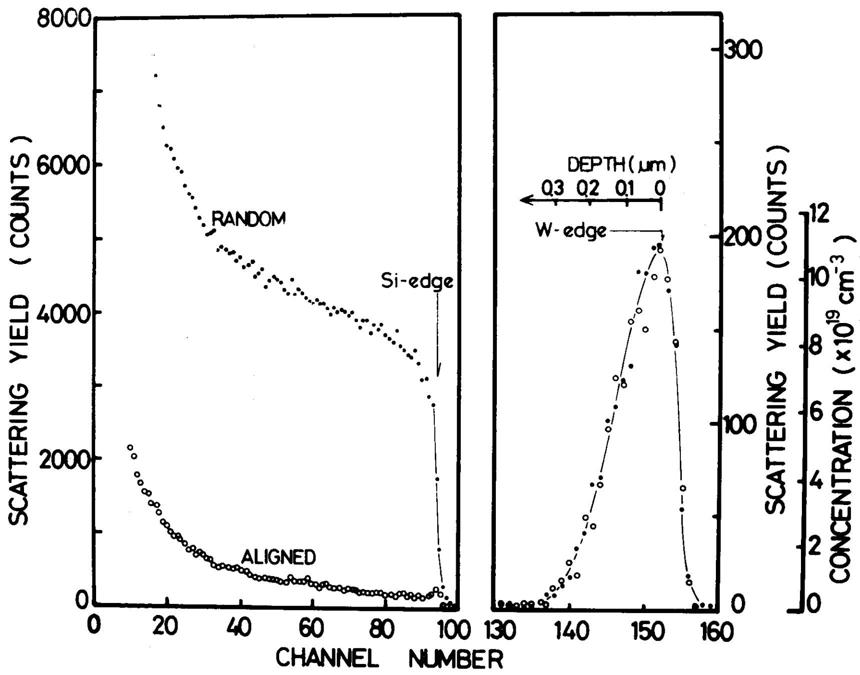


Fig. 3　Backscattering spectra for the case of W overlayers and Si substrates in the random and aligned conditions.

fluence of 5×10^{17} electrons cm^{-2} at 7 MeV without impurity sheets, the conductivity type did not change.

Fig. 3 indicates backscattering spectra in the random and aligned conditions by 1.8 MeV He^+ ions in the case of W(t~0.1mm)/Si irradiated at ~360℃ with a total fluence of $\sim1.0\times10^{18}$ electrons cm^{-2} at 7 MeV. It shows the introduction of W impurities into Si in a depth range of $x<\sim0.3\mu m$ and the maximum W concentration of $\sim1\times10^{20}cm^{-3}$ at the Si surfaca.

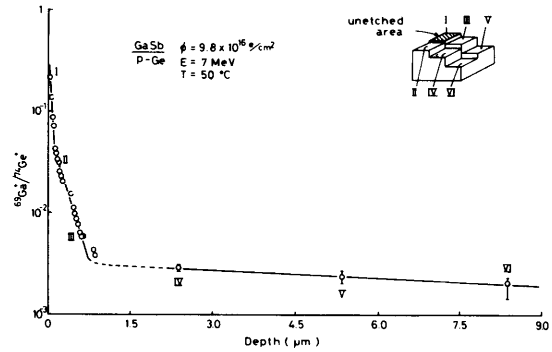


Fig. 4 Impurity (Ga) concentration distribution at deeper depths from the Ge front surface as a function of depth.

The concentration profile of Ga impurity atoms in the experiment of GaSb/Ge is shown in Fig. 4 as a function of depth from the Ge front surfaces. After the bombardment, the Ge surfaces with several different depths d from the original surface were fabricated by chemically etching away different small amounts of Ge from the surfaces, which were partially covered with an organic paint to protect them from successive etching. In order to get each Ge surface of II(d ~0.3μm), III(d~0.6μm), IV(d~2.4μm), V(d~5.4 μm), and VI(d~8.4μm), regions as shown in the inset, respective small amounts of Ge were carefully removed with a new etchant of $1HF+1H_2O_2+4H_2O$ solution at every step. The resultant curve of the intensity ratio of Ga^+ to Ge^+ versus depth in the SIMS measurements is indicated as the continuous curve which is composed of that from each surface. Even at the depth of about 8.4μm, Ga^+ ions were detected.

B. Activation energy of sputtering yield and diffusivities.

In the case of Ge overlayers (t~0.5mm) and Si substrates, the backscattering spectra in the random conditions by 1.4 MeV He^+ ions are shown in Fig. 5(a) for the specimens irradiated at

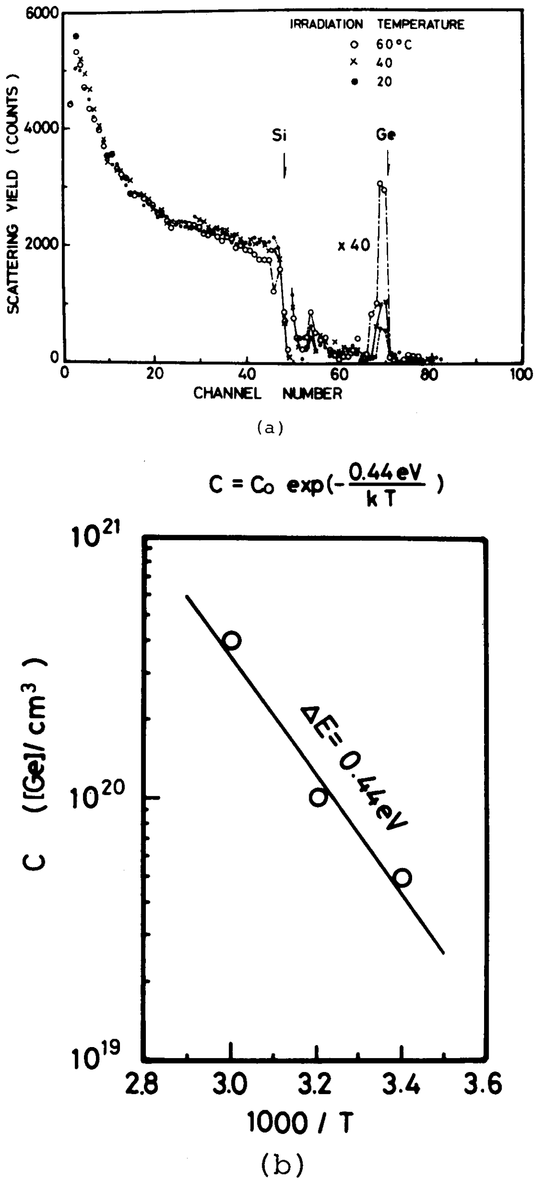
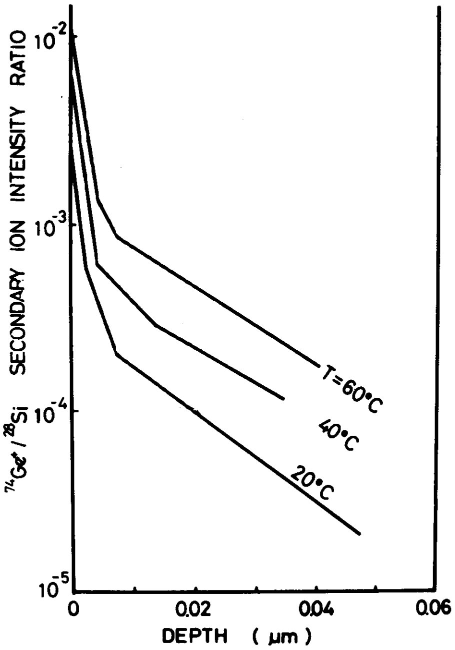
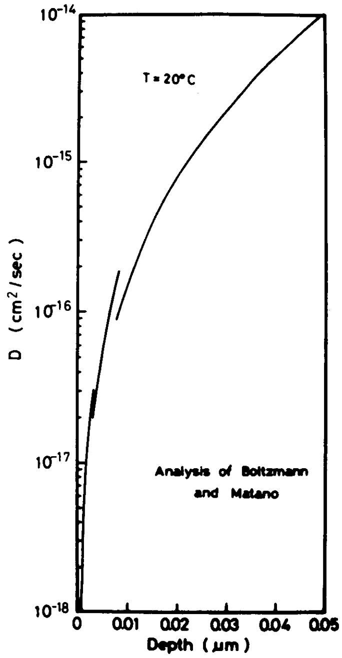


Fig. 5 (a) Backscattering spectra for the irradiated Si in the random conditions at different irradiation temperatures.

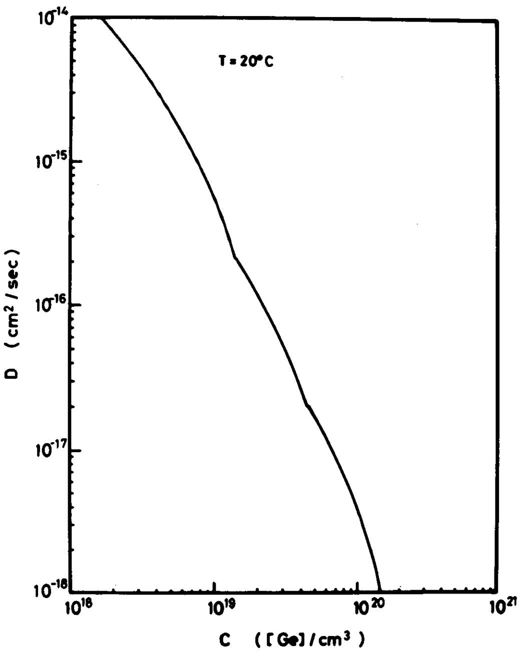
(b) Concentration of Ge impurity as a function of reciprocal irradiation temperature.



(a)

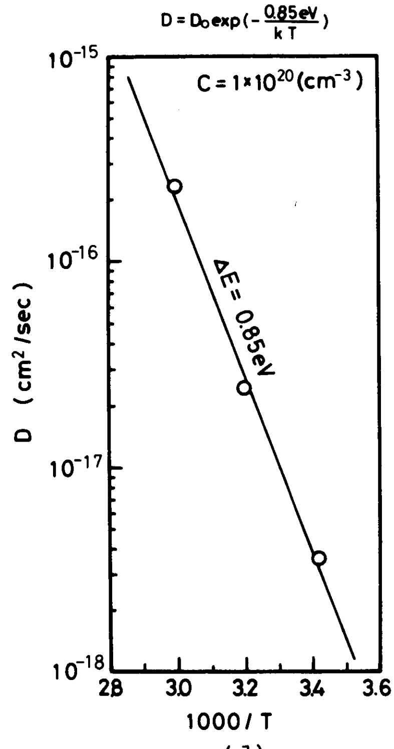


(b)



(c)

$$D = D_0 \exp\left(-\frac{0.85\,eV}{kT}\right)$$



(d)

Fig. 6 (a) Intensity ratios of $^{74}Ge^+$ to $^{28}Si^+$ in Si substrate as a function of depth, from the front surface of Si.

(b) Diffusivity D as a function of depth from the Si surface, and (c) Ge impurity concentration.

(d) Diffusivity of Ge impurity in Si as a function of reciprocal irradiation temperature.

20°, 40° and 60℃ with a total fluence of 5.1×10^{17} electrons cm^{-2} at 7 MeV. The number of counts of Ge peaks in Si increases with increasing irradiation temperature. The expression of the Ge concentration ratio is given by

$$\frac{C_{Ge}}{C_{Si}}=\frac{N_{Ge}}{N_{Si}}\cdot\frac{[S]_{Ge}}{[S]_{Si}}\cdot\frac{P_{Si}}{p_{Ge}} \qquad (1)$$

where C means a concentration, N the number of counts, [S] the backscattering energy loss parameter and P the differential scattering cross sections. The maximum Ge concentrations C_{Ge} estimated from the backscattering spectra in the figure are shown in Fig. 5(b) as a function of reciprocal irradiation temperature. An activation energy of sputtering yield for Ge atoms into Si is estimated to be about 0.44 eV from this figure.

The intensity ratios of $^{74}Ge^+$ ions to $^{28}Si^+$ ions in the case of Ge (t~0.5mm)/Si irradiated by the same conditions as described above are shown in Fig. 6(a) as a function of depth measured from the Si front surface, which is in contact with the overlayer. The SIMS measurements were performed by using the primary ion (O_2^+) beam (diameter 1 mm) with an ion energy of 7 KeV in a 1.5×10^{-7} Torr vacuum. For Si wafers irradiated without impurity sheets, the Ge^+ peaks disappeared. The diffusion profile is not a complementary error function. This suggests that the diffusivity is concentration dependent. The analysis of Boltzmann[46] and Matano[47] is used to obtain the concentration C dependence of the diffusivity D (c). Assuming a constant surface concentration C_o during the entire diffusion, the equation of D(c) in the case of the SIMS measurements is given by

$$D(c)=-\frac{1}{2t'}\frac{\displaystyle\int_{I_{ro}}^{I_r}\frac{X}{(K_sI_r+K_i)^2}\,dI_r}{\left[\dfrac{1}{(K_sI_r+K_i)^2}\,\dfrac{dI_r}{dx}\right]_{I_r}} \qquad (2)$$

where I_i and I_s are the SIMS signal intensities of imprity ions and substrate ions respectively, which are corrected for the natural abundance of the isotope, K_i and K_s are the sputtered ion yield of impurity ions and substrate ions respectively, and I_r is the ratio of I_i to I_s. The calculated values of D(c) at the irradiation temperature of 20℃ are shown in Fig. 6(b) and (c) as a function of depth from the Si surface and impurity concentration, respectively. The value of D(c) decreases with increasing impurity concentration and increases with the depth from the Si surface. The values of D(c) at $x<0.01\mu m$ and $x>0.01\mu m$ for Ge are observed to be $10^{-18}-10^{-16}cm^2sec^{-1}$ and $\sim10^{-16}-10^{-14}cm^2sec^{-1}$, respectively. The value of C_o is estimeted to be $\sim1.4\times10^{20}cm^{-3}$. The resultant plot is mainly composed of three curves. It is suggested that three kinds of species diffuse into the substrate. The diffusivites of D(c) at $c=1\times10^{20}$ cm^{-3} for 20°, 40° and 60℃, which are estimated by the analysis of Boltzmann and Matano from the curves of Fig. 6(a) are shown in Fig. 6(d) as a function of reciprocal irradiation temrerature. From this curve, an activation energy for the diffusivity in Si is obtained to be about 0.85 eV.

C. Electron energy, overlayer thickness and electron fluence dependencies

The relative intensities of Ge impurity atoms are indicated in Fig. 7 as a function of irradiation

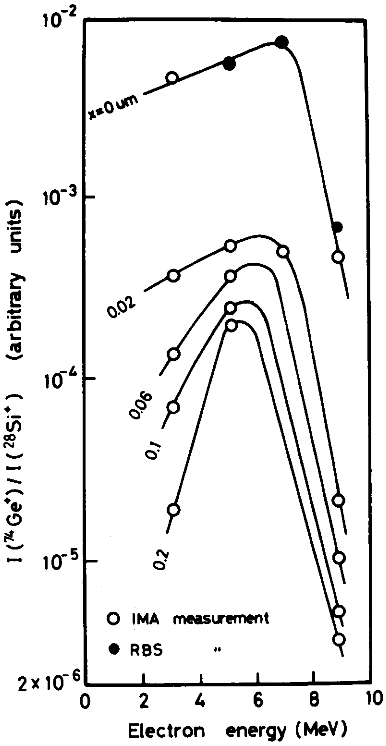
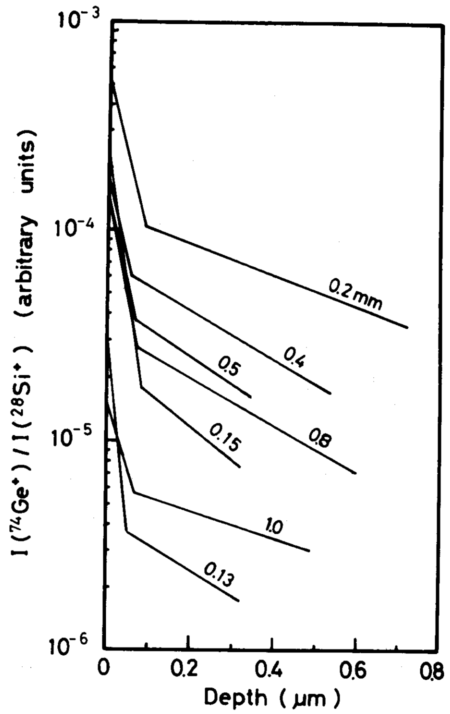
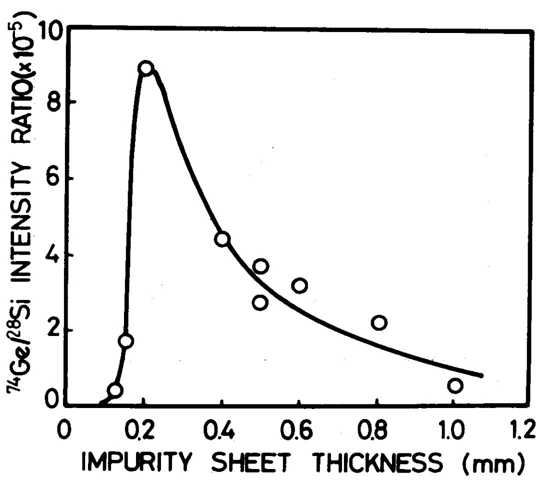


Fig. 7 Intensity ratios of $^{74}Ge^+$ to $^{28}Si^+$ in Si as a function of irradiation electron energy at different depths, from the Si surface.

electron energy at different depths, from the Si surface. The samples were irradiated with a fluence of $\sim 5\times10^{17}$ electrons cm^{-2} at 3, 5, 7 and 9 MeV at 60 ℃, and the thickness of Ge sheets is



(a)



(b)

Fig. 8 (a) Intensity ratios of $^{74}Ge^+$ to $^{28}Si^+$ in Si as a function of depth, from the Si surface at different Ge sheeet thicknesses.

(b) Intensity ratios of $^{74}Ge^+$ to $^{28}Si^+$ in Si as a functaon of Ge sheet thickness.

$\sim$0.5mm. The 5−7 MeV electron irradiation becomes to obtain a maximum sputtering yield.

Fig. 8(a) shows the relative impurity intensities of Ge atoms in Si as a function of depth, from the Si surface at different Ge wafer thicknesses. These samples were irradiated with a total fluence of $\sim 5\times10^{17}$ electrons cm^{-2} at 7 MeV. The relative impurity intensities of Ge atoms at a depth of 0.2μm in Si are indicated in Fig. 8(b) as a function of Ge overlayer thickness. At the thickness of $\sim$0.2mm, the intensity ratio of $^{74}Ge^+$ ions to $^{28}Si^+$ ions becomes a maximum value.

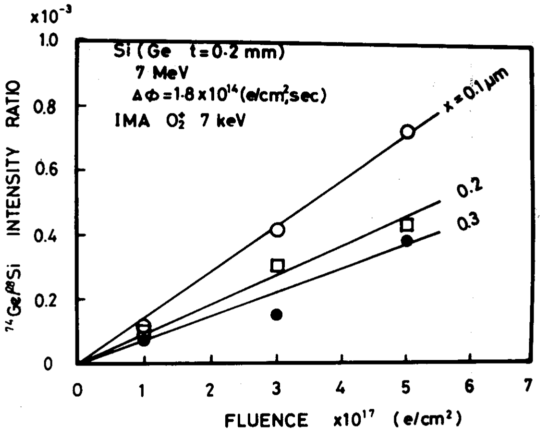


Fig. 9 Intensity ratios of $^{74}Ge^+$ to $^{28}Si^+$ as a function of electron fluence at different depths, from the Si surface.

Fig. 9 shows the ratio of $^{74}Ge^+$ to $^{28}Si^+$ in the case of Ge/Si as a function of electron fluence at different depths, from the Si surface. In the experiments the fluence rate is about 1.8×10^{14} electrons $cm^{-2}sec^{-1}$. The density of impurity atoms is directly proportional to electron fluence.

D. Surface diffusion

The surface of the Si substrate with an area of 20×20 mm^2(t$\sim$0.35mm) was covered partially by an overlayer of Ge wafer with an area of $\sim 5\times5$ mm^2 (t$\sim$0.26mm) as shown in the inset of Fig. 10. When the surface of Ge sheet was bombarded with a fluence of $\sim 5.3\times10^{17}$ electrons cm^{-2} at 7 MeV and at 40℃, the Ge impurities were introduced all over the Si surface. The intensity ratios of $^{74}Ge^+$ ions to $^{28}Si^+$ ions are shown in Fig. 10 as a function of depth measured from the Si front

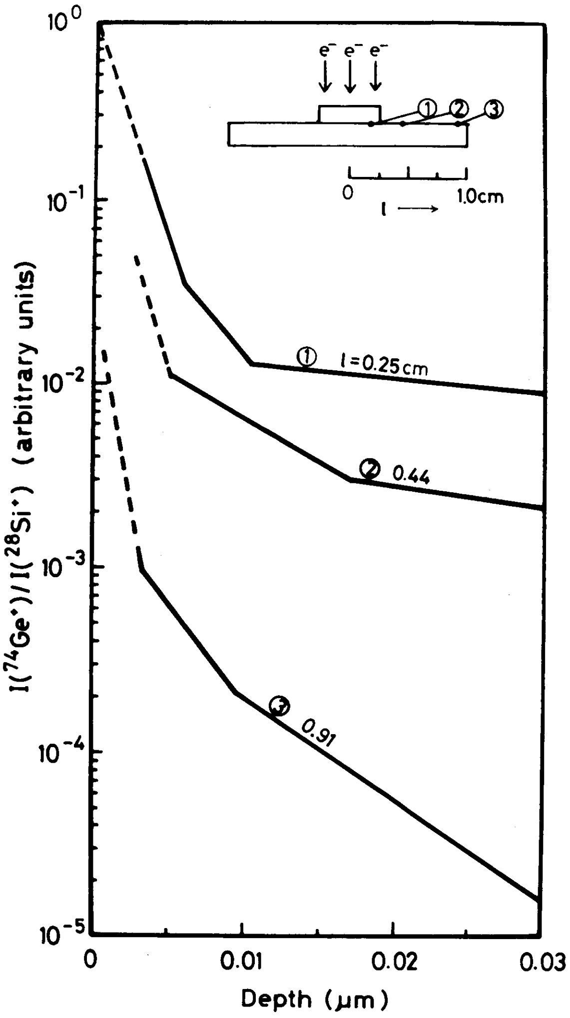


Fig. 10 Intensity ratios of $^{74}Ge^+$ to $^{28}Si^+$ ions in Si substrate as a function of depth, from the front surface of Si at different distances from the center of the overlayer surface.

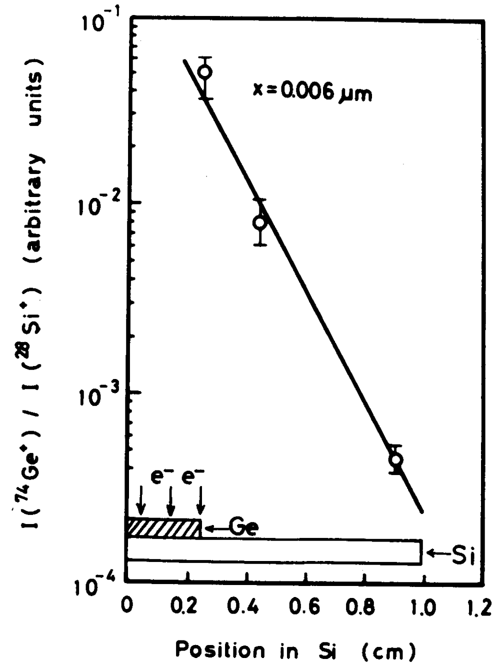


Fig. 11 Intensity ratios of Ge^+/Si^+ as a function of distance from the center of the overlayer surface.

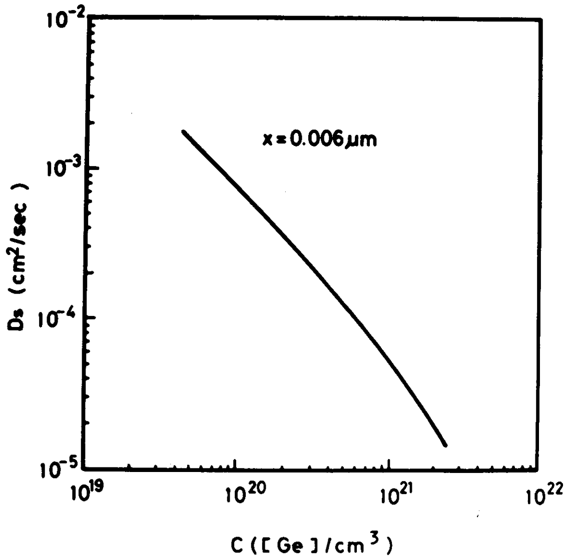


Fig. 12 Calculated diffusivities D_s of the surface diffusion as a function of impurity concentration.

surface, which is partially in contact with the overlayer, at different distances of 2.5, 4.4 and 9.1mm from the center of the overlayer back surface. The SIMS measurements were performed by using the primary ion (O_2^+) beam (diameter~1 mm) with an ion energy of 7 KeV in a 1.5×10^{-7} Torr vacuum, with an accuracy of within 10%. Even at a distance of 9.1mm from the overlayer, Ge^+ ions are detected. Fig. 11 indicates the intensity ratios of Ge^+/Si^+ as a function of distance from the center of the overlayer region at a depth of 0.006μm from the Si surface. The calculated values of $D_s(c)$ at the surface are shown in Fig. 12 as a function of impurity concentration. For the calculation, 1920sec of the irradiation time is used as the diffusion time t'.

The values of $D_s(c)$ decrease with increasing impurity concentration and are estimated to be $2\times10^{-3}-10^{-5}cm^2sec^{-1}$. The value of C_0 is obtained to be $2\times10^{21}cm^{-3}$. In the case of 20℃, 60℃ and 200℃ irradiation, the similar experimental results were obtained to be

$$D_s(c) \simeq 10^{-3}-4\times10^{-7}cm^2\cdot sec^{-1}$$
$$C_0\simeq3\times10^{20}-2\times10^{21}cm^{-3} \quad (3)$$

at 20°, 40°, 60° and 200℃.

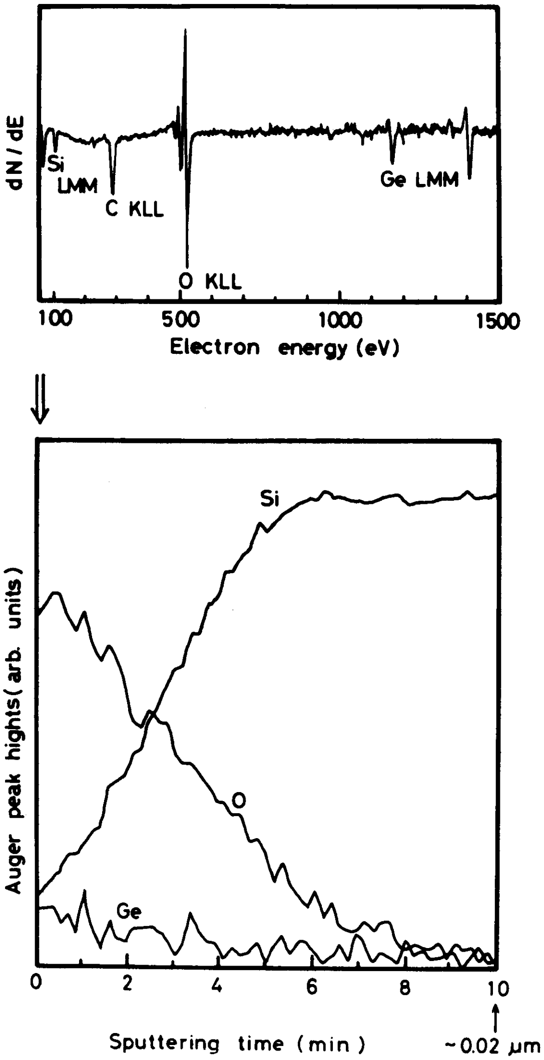


Fig. 13 Observed Auger signal ratio of Ge (LMM peak-peak), O(KLL peak-peak) and Si (LMM peak-peak) as a function of sputter-etching time from the Si surface, together with the Auger electron spectrum.

Auger electron spectroscopy (AES) was combined with ion sputtering to measure the concentration profiles of Si atoms, Ge impurities and oxygen atoms. Fig. 13 shows the observed Auger signal intensities of Ge (LMM peak-peak), O (KLL peak-peak) and Si (LMM peak-peak) as a function of sputter-etching time from the Si surface, together with the Auger electron spectrum. The Si surface under the Ge overlayer of the same sample as mentioned in Fig. 10 was used in the experiments. The AES measurements were performed by an incident electron beam (diameter $\sim0.3\mu m$) at 10 KeV energies with a current of $2\times10^{-7}A$ and a pressure of 3×10^{-9} Torr. The sputter-etching was done by the ion (Ar^+) energy of 3 KeV with an Ar pressure of 2×10^{-5} Torr. This figure indicates the presence of an SiO_2 layer of $0.01\mu m$ thickness after the irradiation. Then the concentration profile near the surface in Fig. 11 may represent the diffusion SiO_2 or at the Si surface. Whenever a charged particle (a high energy electron) loses energy in a solid, electron-hole pairs (ehp) are produced.

The rate of generation g of electron-hole pairs (ehp) per unit time by an incident electron beam is given by[48]

$$g=\frac{1}{\Sigma}\cdot\frac{dE}{dx}\cdot\frac{d\phi}{dt} \quad (4)$$

where Σ is the energy for the formation of ehp in Si (3.8eV)[49], $dE/dx\simeq1.6MeV\,cm^2g^{-1}$ electron^{-1} [50] are the energy loss per cm of path by a fast electron in Si and $d\phi/dt$ is the irradiation rate. Irradiation at a rate of 2.5×10^{14} electrons cm^{-2} sec^{-1} would result in $g\simeq2.5\times10^{20}$ ehp's $cm^{-3}\,sec^{-1}$ for Si. The ehp generetion produces an ehp concentration of $C=g\tau$, where τ is the excess carrier lifetime. Actually τ is difficult to evaluate, since it is very sensitive to the amount of defects. Assuming that the Ge concentration profile of Fig. 11 may be caused by a distribution of the electron-hole pairs, τ is roughly estimated to be about 10^{-3} sec. Thus, $c\simeq2.5\times10^{17}cm^{-3}$ for Si. As the resistivity of the substrate region that are not covered with Ge overlayer and unirradiated by electrons is $25-50\Omega\,cm$, there are gradients of Fermi energy μ (corresponding to chemical potential) along the surface l for the boundary of electron irradiated regions. As Ge atoms at interstitial sites may be charged, such gradients may produce a drift of surface atoms with an average velocity[51] given by the Nernst-Einstein relation $V = D_s/KT \cdot \partial\mu/\partial l$, where D_s is the coefficient of surface diffusion. Also when such a number of conduction electrons and/or holes in Si recombine at defects via non-radiative transition, mobility enhancement of impurity atoms may be caused by the energy released in these processes.

The activation energy for surface diffusion is related to the strength and localization of the bonding of the sorbate to the surface[52]. For example, a neutral atom on the surface of an ionic solid may in many cases move relatively freely[53], as there is no strong bond. In some cases, although the heat of adsorption is substantial, the activation energy for diffusion can be low. In the present experiments, also the surface diffusion may be expected.

E. U-shaped diffusion profile

The surface of the Si substrate with an area of $\sim 15 \times 15$ mm² ($t \simeq 0.5$ mm) was covered partially by an overlayer of Ge sheet with an area of 5×5 mm² ($t \simeq 0.26$mm) as shown in the inset of Fig. 14. When the surface of Ge sheet was bombarded with a fluence of $\sim 10^{18}$ electrons cm^{-2} at 7 MeV and at 200℃, the Ge impurities were doped even in the back surfaces of the substrate. The intensity ratios of Ge^+/Si^+ at the different positions of ①, ② at the front surface and ③ at tha back surface decrease with increasing a distance from the center of the overlayer regions. The concentration-dependent diffusivities for Ge in Si are obtained for the diffusion profiles at the positions of ① (front surface) and ④ (back surface) by the analysis of Boltzmann and Matano as shown in Fig. 15. The value of $D_v(c)$ for the volume diffusion decreases from 2×10^{-14} to 3×10^{-17} cm^{2}sec^{-1} with increasing impurity concentration. The resultant plot is mainly composed of two curves. It is suggested that two kinds of species diffuse into the substrate. The values of C_0 for the front and back surface are 3×10^{20} and 1×10^{19} cm^{-3}, respectively. The volume diffusivities indicate

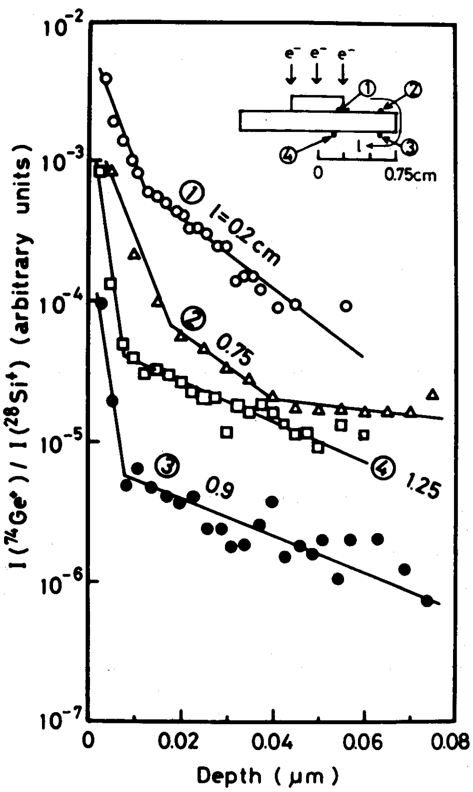


Fig. 14 Intensity ratios of Ge^+/Si^+ in Si substrate as a function of depth from the Si surface at different distances for the front and back surface.

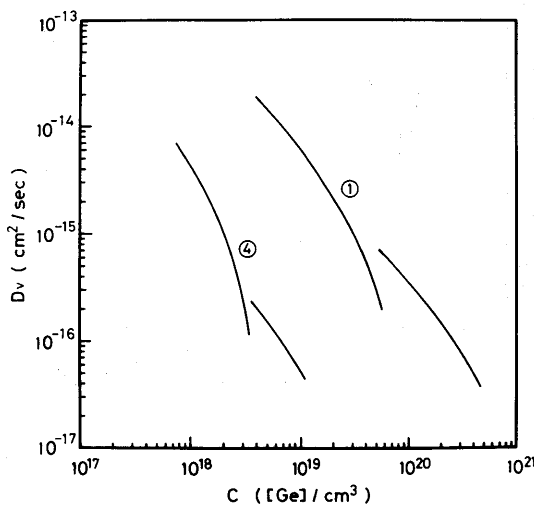


Fig. 15 Calculated diffusivities D_V of the volume diffusion as a function of impurity concentration for the front ① and back ④ surface.

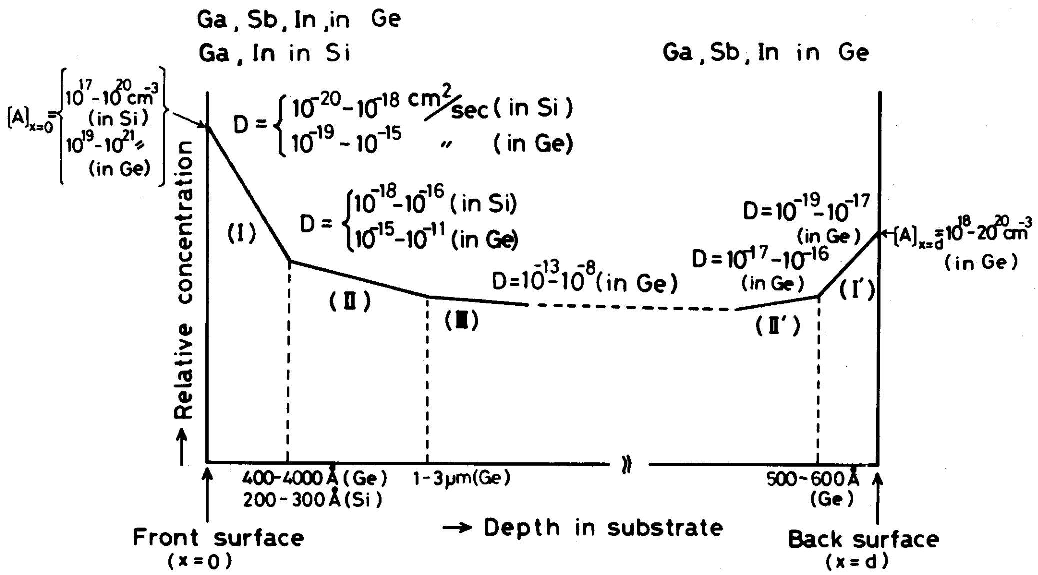


Fig. 16 Impurity distribution in substrate (Ge, Si) as a function of depth from both the front and back surfaces with different impurity atoms.

the strong variation with impurity concentration. A large difference of the data of ① and ④ may be caused by a variation of the concentrations at the front and back surface.

Fig. 16 shows the experimental results of the typical impurity profiles of having three kinds of diffusivities in Ge(Si) at 300 K for depth region of I, II, and III with surface impurity concentration of $[A]_{x=0}$ at the front surface and $[A]_{x=d}$ at the back surface.

The values of D_s are much larger than that of D_v. The recoil-implanted impurities from the overlayers diffuse from the front to back surface of the substrate through the surfaces, and then the impurities at the back sueface rediffuse into the specimen from the back surface by the value of $D_v(c)$. As s result of the diffusion process, the depth distribution of impurities in the substrate would give rise to a U-shaped diffusion profile.

As another possible mechanism of U-shaped diffusion profile, D_s is supposed to be a constant value and the diffusion process for D_v is conside-red as follows[43]. For simplicity, it is assumed that a diffusion process is mainly composed of two streams of substitutional (A_{sub}) and interstitial (A_i) sites with different constant diffusivities, and there is an exchange of flow between them. The diffusivities of A_i is much higher than that of A_{sub}. Thermal equilibrium between A_{sub} and A_i may be established via Ge self-interstitials accor-ding to the kick-out mechanism[54] $A_{sub} + I \underset{K_2}{\overset{K_1}{\rightleftarrows}} A_i$, where I is self-ineterstials, and K_1 and K_2 are reaction constants. The resulting impurity concen-tration profile is obtained from a solution of the set of equations continuity[43]. The theoretical depth distributions of the total impurity $[A]=[A]_i+[A]_{sub}$ and $[I]$ are qualitatively in agreement with the experimental results[43]. The defects introduced by electron-beam doping are easily annealed at lower temperatures[44].

References

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