COINCIDENCE DOPPLER BROADENING POSITRON ANNIHILATION SPECTROSCOPY IN DEFECTS IN IRON AND SILICON

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ABSTRACT

Coincidence Doppler broadening (CDB) method in positron annihilation spectroscopy has been applied to chemical state analysis of the vacancy-impurity complexes in silicon and iron implanted with various ions. In Si implanted with oxygen 2x10¹⁵/cm² at 180 keV and hydrogen 1x10¹⁶/cm² at 60 keV, the defect structure has been discussed. CDB spectra reflect the character of elements coupled with vacancies very well, and enables us to estimate the number of impurities in the defects with combination of positron lifetime measurement. In Cu ion (5x10¹⁵/cm² at 140 keV) implantation to Fe, it has been directly proved that vacancies and Cu atoms aggregate and that the inner wall of V-Cu complexes is covered with Cu atoms.

KEYWORDS

Positron annihilation spectroscopy, Coincidence Doppler broadening, Vacancy-impurity complexes, Chemical analysis, Silicon, Iron

INTRODUCTION

Positron annihilation spectroscopy is one of the most powerful techniques for studying the defects in solids and gives information on size and quantity in open-volume type defects. It is very important to observe the behavior of defects coupled with impurities because it is strongly dependent on a kind of impurity. Positron lifetime and shape of annihilation γ-rays spectrum strongly depend on them, although it is very difficult to extract the information of impurity from their measurements. A coincidence Doppler broadening (CDB) method in positron annihilation spectroscopy has been recently developed to carry out the chemical analysis of defects [1,2,3]. The positrons trapped at vacancy-impurity (V-I) complexes annihilate electrons due to impurity. Annihilation with core electrons gives larger Doppler shifts compared with valence electrons, so that it is possible to identify the impurity by analyzing the high electron momentum region. The CDB method improves the peak to background ratio in the annihilation spectrum to around 10⁵ and fine structures due to core electrons...
from impurity atom can be discussed. In this paper, with a combination of positron lifetime measurements, CDB method has been applied to study the defects in silicon and iron implanted with various kinds of ions.

EXPERIMENTALS

The samples were subjected to ion implantation and the subsequent annealing, and the defective layer was formed near the surface. The O ion implantation to CZ-Si wafer substrate was carried out at 180 keV with a dose of $2 \times 10^{15}$/cm$^2$, and the H ion at 60 keV with a dose of $1 \times 10^{16}$/cm$^2$. The iron sheet were implanted with Cu at 140 keV with a dose of $5 \times 10^{13}$, $10^{14}$, $10^{15}$/cm$^2$. These implanted samples were annealed at various temperatures for 30 min. in a vacuum of $1 \times 10^{-5}$ Torr. CDB measurements were performed using the low energy positron beam facility at NIRIM providing $1 \times 10^5$ e$^+/s$ in the energy from 0 to 30 keV. Around $1.5 \times 10^7$ counts were accumulated for each spectrum, which was the diagonal cross section of the two-dimensional spectrum with a width of $2m_0c^2 - 1.2$ keV < $E_1 + E_2$ < $2m_0c^2 + 1.2$ keV. The data are exhibited in terms of ratio-differences curves, in which the small change at high momentum region can be distinguishable. As a reference in Si, a spectrum of divacancy, $V_2$, induced by self-ion implantation ($2 \times 10^{14}$/cm$^2$, 100 keV) to Si, was used, while one of a defect-free Fe was used in Fe. Conventional Doppler broadening (S parameter) measurements and positron lifetime ones using a positron beam were also employed. The S parameter is defined as the ratio of the counts in a central region of the annihilation photopeak to those in the whole one and normalized to the value for bulk Si or Fe. The value of S generally increases due to an increase of the overlap of the positron density with (low-momentum) valence electrons when the positrons are trapped at vacancy-type defects.

RESULTS & DISCUSSION

Si implanted with O ions

An understanding of the behavior on oxygen-related defects in Si is essential to the fabrication of CZ-Si wafers, in which an oxygen concentration of around $10^{18}$/cm$^3$ is introduced from the SiO$_2$ crucible used in the crystal-growth process. And the novel semiconductor substrate named SIMOX wafer has been proposed and the internal SiO$_2$ layer is formed between thin single crystal Si layer and Si substrate. Heavily ion implantation more than $10^{17}$/cm$^2$ is employed in SIMOX fabrication, so that much attention has been paid to oxygen-related defects in Si. Some positron studies on them has been carried out and it has been reported that very low S value and short lifetime are responsible for oxygen-related defects in Si [4,5,6].

Figure 1 shows S-E curves for Si implanted with $2 \times 10^{15}$ O ions/cm$^2$ at 180 keV and the samples after annealing. The mean projected range is around 380 nm, so that positron lifetimes at 5 keV stand for the information on the most defective layer. In the as-implanted sample, larger S is observed and the positron lifetime of 298 ps is longer that that, 219 ps, of the bulk and

![Figure 1](image-url)
corresponds to that of divacancy in Si. In annealing at 600°C, drastic change takes place. Value of S is still large below positron energy of 2 keV, while that of S decreases in the region of more than 2 keV, and becomes lower than that of the bulk. If positrons annihilate electrons of matrix Si atoms, S value should not be lower than that of the bulk. This result suggests that a part of positrons annihilates electrons of the different kinds of atoms with matrix ones. The origin of lowering in S is considered to be due to the formation of V-O complex defects. The positron lifetime at 5 keV is estimated to be 330 ps (intensity: 97%), which corresponds to V₄, indicating that the defects formed are open-volume type. An anneal at 800°C gives rise to the minimum S, 0.93, at 6.5 keV and the long lifetime of 322 ps (97%). These results show that the size of open-volume is unchanged, while a fraction of positrons which annihilate electrons of non-Si atoms increases. The value of S strongly depends on the dose of oxygen implanted, so that it is concluded that vacancy-oxygen complexes are formed, and that positrons trapped at them give very low S due to electrons of oxygen.

To clarify their defect structures, CDB measurements at the positron energy of 5 keV have been carried out and the results are exhibited in Fig. 2. The CDB spectrum of the as-implanted sample does not coincide with that of V₂ in Si. The intensity in the range from 10 to 20 mrad due to oxygen atoms becomes larger, while that around 0 mrad is nearly unity. It is found that oxygen atoms are involved in the defects induced only by ion implantation and the size of the defects is almost same to V₂. As the annealing temperature rises, their intensity is increased, indicating that the number of oxygen atoms involved in the defects increases more and more. In combination of positron lifetime and CDB spectra, the following model on V-O defects can be summarized.

(1) Up to 500°C: The positron lifetime is around 300 ps and the CDB spectrum shows a slight large intensity in the range of 10 to 20 mrad. It is known that, in the relation of positron lifetime with the defect size, the lifetime of V₂I₂ complex is same to that of V₄₋₂ clusters and the lifetime of 300 ps coincides with that of V₂ in Si. It is, therefore, concluded that the formation of V₃O is dominant in the as-implanted sample and the samples annealed up to 500°C.

(2) 600°C: The lifetime is around 320 ps, which coincides with V₄ in Si, and the intensity in 10-20 mrad in the CDB spectrum is increased. Hence the defects formed are considered to be V₆O₂ complexes, in consequence of a combination of two V₃O.

(3) 800°C: The lifetime is unchanged, compared with that of the sample annealed at 600°C, and the intensity in 10-20 mrad in the CDB spectrum is further greater. The magic numbers of vacancy cluster are well known to be 4, 6, 10, etc., so that the formation of V₁₀O₆ is acceptable.

**Si implanted with H ions**

The behavior of H atoms is very complicated in any materials. Hydrogen atoms are easily terminated at the dangling bond of defects in Si and stabilize them. These H property is utilized in amorphous Si:H and delamination of Si wafer. From the fact that S value for the Si implanted with H is similar to that for the bulk, it had been said that positrons were insensitive to H-related defects in

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**Figure 2:** CDB spectra for the O ion (180 keV, 2x10¹⁵ /cm²) implanted Si and the samples annealed.

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Si [7]. But the authors have found that the lifetime for the H-terminated defects is longer than that for the bulk and that positrons are trapped at them [8]. In this section, the behavior of H-related defects in Si is discussed from the CDB spectra.

The S-E curves for the H-implanted Si (1x10^{16} H/cm² at 60 keV) and the annealed samples are shown in Fig. 3. For the as-implanted sample, large S and long lifetime of 280 ps (100%) at the positron energy of 7 keV are observed and the open-volume type defects are induced. The S-E curve for the sample annealed at 400°C returns to that for the virgin Si. This result can be interpreted with no defects in the sample, although the lifetime is still long and estimated to be 283 ps (100%). By annealing at 600°C, S value increases again and long lifetime component of 445 ps (62%) is taken, indicating that large vacancy clusters such as V₁₀ are formed.

The CDB spectra at the positron energy of 6 keV are exhibited in Fig. 4. For the as-implanted sample, the intensity in the region of 5 to 15 mrad is larger than that for V₂ in Si. Annealing up to 400°C results in appearance of broad peak around 8 mrad. It is, therefore, considered that the H-terminated defects in Si are responsible for this peak and that the number of H coupled with vacancy is increased up to 400°C.

The defect structure in this system is considered. The above-mentioned results indicate that the defect size is almost unchanged and H atoms are terminated to vacancies up to 400°C. Divacancy in Si is mobile around 230°C, but H termination prohibits the migration and the clustering of defects. If H terminated to defects do not affect the positron lifetime very much due to the small size, the implantation-induced defects may be attributed to be V₂H or V₂H₂ complexes, and the defects formed at 400°C V₂H₆.

It is very difficult to discuss the chemical state of defects coupled with impurities from only the positron lifetime and line shape parameter such as S, but it has been found that CDB technique enables us to estimate the number of impurities in the defects. For more detail discussion, theoretical calculation is required.
**Fe implanted with Cu ions**
The presence of impurity also results in the complexity in defect behavior in metal and CDB method is useful to study the interaction with impurity aggregations and vacancy. In this work, the reaction of Cu with vacancy, induced by Cu ion implantation to Fe, has been investigated. Hori et al. [9] suggested from the lifetime measurement the nucleation of copper precipitates was coupled with vacancy. Nagai et al. [10] reported that very-dilute Fe-Cu system irradiated by fast neutrons was studied by CDB technique and that ultrafine Cu precipitates were responsible for irradiation-induced embrittlement of RPV steels.

Figure 5 show the S-E curves for the Fe samples implanted with $5 \times 10^{13}$, $5 \times 10^{14}$, and $5 \times 10^{15}$ Cu$^+/cm^2$ at 140 keV and the samples annealed at 300°C. S value near surface is large in all of the samples, indicative of the formation of vacancy-type defects. Little difference between $5 \times 10^{13}$ and $5 \times 10^{14}$ Cu$^+/cm^2$ samples is observed, while S is lowered in $5 \times 10^{15}$ Cu$^+/cm^2$ sample. Annealing at 300°C gives rise to the sudden lowering of S and it seems that the defects anneal out.

The CDB spectra of these samples at the positron energy of 3 keV are displayed in Fig. 6. No peaks appear for the $5 \times 10^{13}$ and $5 \times 10^{14}$ Cu$^+/cm^2$ samples. In less than $5 \times 10^{14}$ Cu$^+/cm^2$ samples, the behavior of defects is very similar to that in pure Fe and we may consider only the simple vacancy-type defects in these systems. The broad peak around 22 mrad is observed in both of the $5 \times 10^{15}$ Cu$^+/cm^2$ sample and the annealed, and coincides with that of pure Cu [10], indicating that positrons annihilate electrons due to Cu. Further, the intensity of the peak increases by annealing at 300°C. These results are interpreted by the aggregations of vacancies and Cu atoms. Vacancies in Fe easily diffuse even at room temperature, and are consequently trapped with Cu. Due to the high binding energy between vacancy and Cu in Fe, V-Cu complexes migrate and are stabilized by a formation of large clusters. It is considered that the inner wall of micro voids is covered with Cu atoms, since Cu has a lower surface energy than Fe.

![Figure 5: S-E curves for the Cu ion (140 keV, 5x10^{13}, 5x10^{14}, 5x10^{15} /cm^2) implanted Si and the samples annealed.](image1)

![Figure 6: S-E curves for the Cu ion (140 keV, 5x10^{13}, 5x10^{14}, 5x10^{15} /cm^2) implanted Si and the samples annealed. The symbols are identical to those of Fig. 5.](image2)
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