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Mössbauer study of iron in β-silicon nitride – effects of heat treatment and γ-irradiation

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Mössbauer spectra of iron in β-silicon nitride, prepared from a mixture of silica and carbon and from metallic silicon, were measured under various conditions. Iron was introduced into the crystal as an impurity in carbon, and where necessary was further doped by means of thermal diffusion mainly in a nitrogen atmosphere. As a result, the spectra were observed to change in a complicated way, including a sudden change when the samples were highly exposed to γ-rays or heated at high temperatures. In addition, they were found to show significant ageing at room temperature. All these results were dependent on the doping procedure. Also, in the processes of doping different kinds of species containing iron were found to form inside and outside the crystal depending on the state of iron before the doping, even though the doping itself was performed for all the samples under almost the same conditions. Explanations are given for the former results in terms of dynamics of the iron and silicon, along with residual carbon atoms and vacancies which were left behind by those atoms in the heating process or newly generated in the irradiation process.

1. Introduction

In recent years, considerable interest has been paid to silicon nitride due to its outstanding properties in nuclear, as well as industrial applications. It is known widely that the properties are strongly influenced by the presence of a small amount of iron. In order to throw light upon the mechanism, we have studied the state of iron contained in α- and β-silicon nitrides with the Mössbauer and Raman effects [1]. From the results obtained, the conclusion has been drawn that the iron in question is in the trivalent state and substitutionally located at isolated and two neighbouring silicon sites. For the samples used, iron was introduced into the crystal through the following two processes: 1. as an impurity in a starting material of its preparation, and 2. by subsequent thermal diffusion after the preparation. For simplicity, hereafter we designate β-silicon nitride just prepared through the process 1 as the original sample. And, the word "dope" means introduction through process 2. The previous work has shown that the iron gives rise to three Mössbauer lines independent of the processes.

Afterwards, in the measurements on the original sample containing a much greater amount of iron, we noticed that the three lines had displayed a marked change on annealing at an elevated temperature. Further, we found that after doping with ^{57}Fe, of these lines the highest energy line intensity depended strongly upon whether or not the sample was annealed prior to doping. For the

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applications of silicon nitrode, it seems important to study the effects of heating at high temperatures, and radiations of high dose upon β-silicon nitride, which is more stable than the α-type. However, little is known about lattice defects produced by such treatments. Since the three Mössbauer lines arising from the substitutional iron were already identified, the utility of the Mössbauer effect is thought to be effective for this purpose.

For these reasons, detailed studies were conducted on the Mössbauer spectra of β-silicon nitride, which was doped with ^{57}Fe through both processes and then treated in the above ways. As a result, we observed that besides the foregoing changes, the spectra varied in a complicated way including a sudden change upon heating or irradiating with γ-rays. We also found that different species such as ions, alloys and fine particles, each consisting of iron, were produced depending on the state of preexisting iron in the crystal, although the ^{57}Fe-doping was performed for the samples under almost the same conditions. Analysis of the spectra obtained allowed us to give qualitative explanations for them in terms of dynamics of the iron ions and silicon ions which are generated by γ-rays, combined with a motion of silicon vacancies introduced by heat treatment or γ-irradiation.

The object of this paper is to describe these experimental results and to give explanations for some of them.

2. Experimental details

A starting material used in preparing β-silicon nitride was a mixture of 71.4% silica (99.31% purity), 28.6% carbon (containing 1.17% iron) and an organic binder. This mixture was heated at 1520° C in the flowing nitrogen (99.999% purity) at a rate of $1220\,\mathrm{ml\,min^{-1}}$. Besides, for special purposes, β-silicon nitride was prepared from metallic silicon in a nitrogen atmosphere. The crystal structure of the resulting powdered substances was checked by an X-ray diffraction method.

The doping of ^{57}Fe was carried out by heating β-silicon nitride mixed with $^{57}Fe_2O_3$ (95.17% purity) at 1150° C for 4 to 5 h in a high-pure nitrogen atmosphere of about 1 atm sealed in quartz ampoules, and then quenching to room temperature. In a few cases, the doping was also performed in air and in a high-pure argon atmosphere. Mössbauer measurements were made at room temperature using ^{57}Co in a copper matrix as a source. When it was necessary to distinguish whether the spectra under consideration arose from iron inside or outside the crystal, the samples were washed in boiling 18% HCl solution and then filtered, the two treatments being repeated several times. They made it possible to remove a great amount of iron which was adsorbed on the crystal surface or simply mixed in the samples. Exposure to radiation was made at room temperature with γ-rays from a ^{60}Co-source with an exposure rate of the order of $10^5\,\mathrm{R\,h^{-1}}$.

3. Results

The Mössbauer spectrum of the original sample is reproduced in Fig. 1a, which reveals the three lines at the central portion and two extra lines due to metallic iron superimposed on their wings. Fig. 1b displays the Mössbauer spectrum recorded immediately after the original sample was doped with ^{57}Fe. It consists of three lines located at the central portion and of extra lines, which are clearly due to unreacted Fe_2O_3, appearing on both sides of them.

Fig. 2a shows the Mössbauer spectrum obtained after the original sample was annealed to remove residual carbon atoms at 600° C for 1 h in air, then kept at room temperature for 438 days and lastly treated with the HCl solution. The spectrum has only two peaks, and its features differ from those of the spectrum of Fig. 1a. A spectrum like this was also observed immediately after annealing. When the sample showing this spectrum was doped with ^{57}Fe in a nitrogen atmosphere, we obtained the Mössbauer spectrum as indicated in Fig. 2b, which appears similar to the spectrum of Fig. 1a. The intensities of the three lines diminished equally and gradually while the sample was stored at room temperature. As an illustration, the spectrum for storage of 91 days is given in Figs. 2c. Fig. 2d shows the Mössbauer spectrum taken after the above sample was further stored for 402 days at room temperature. It possesses a large asymmetry and differs from all of the spectra already described. Fig. 2e depicts the Mössbauer spectrum measured after the sample showing the spectrum of Fig. 2a was stored for 475 days at room temperature. It is likely to consist of at least two doublets.

Fig. 3a shows the Mössbauer spectrum obtained when the sample showing the spectrum of Fig. 2a was doped two times with ^{57}Fe with an interval of 335 days in a nitrogen atmosphere. At first sight, the spectrum seems to be very complex because of

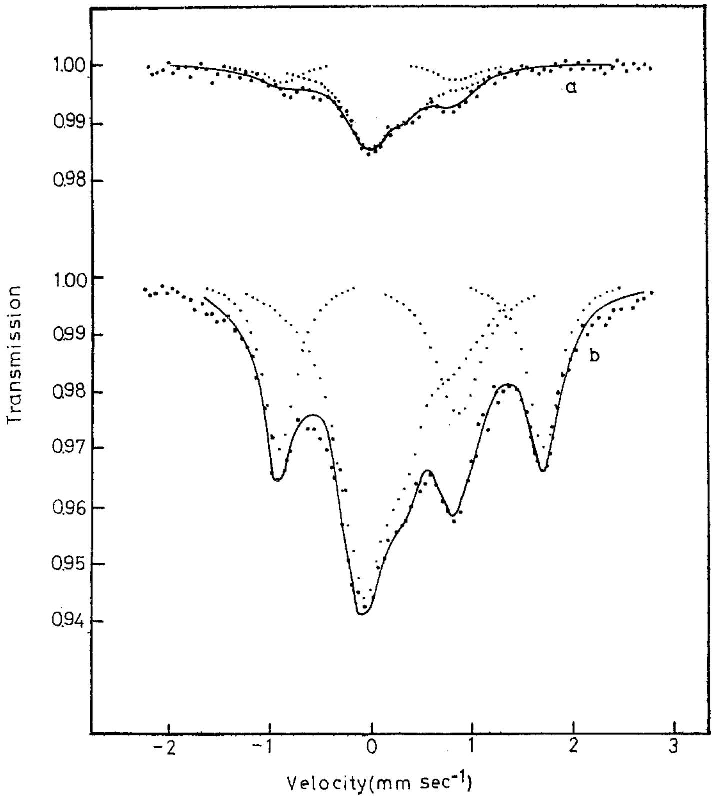

Figure 1 Mössbauer spectra of the original sample measured (a) before, and (b) after ^{57}Fe-doping.

overlapping six-line patterns. This spectrum was varied to that of Fig. 3b, when the sample was heated at 870° C for 20 h in a nitrogen atmosphere. Besides six-line patterns, the latter spectrum appears to possess a single line, as evident from the presence of a strong peak at the central portion. Treating the sample further with the HCl solution, we observed a spectrum similar to that of Fig. 2d, as presented in Fig. 3c.

Fig. 4a is the same as Fig. 2e. When this sample was doped with ^{57}Fe at 1150° C for 5 h in a nitrogen atmosphere, we obtained the Mössbauer spectrum of Fig. 3a. Fig. 4c shows the Mössbauer spectrum taken after treating the above sample with HCl solution. It appears to consist of three broad lines that are distinct from the three lines of Fig. 1a. Subsequent heating of the sample at 1150° C for 5 h in a nitrogen atmosphere caused no changes in the spectrum, but additional annealing at 1150° C for 8 h in an argon atmosphere converted it into the spectrum revealed in Fig. 4d. This spectrum is very similar to that of Fig. 4a.

The Mössbauer spectrum of Fig. 5a is the same as that of Fig. 2c. Fig. 5b shows the Mössbauer spectrum of ^{57}Fe doped in the sample showing the spectrum of Fig. 5a. The spectrum is complicated because of six-line pattern superimposed on a broad central peak, as in the cases of Figs. 3b and 4b. Fig. 5c reveals the Mössbauer spectrum recorded after the above sample was treated with the HCl solution. It is likely that this spectrum consists primarily of three lines like those shown in Fig. 1a, and some very weak lines are additionally seen on both sides of them.

Fig. 6a displays the Mössbauer spectrum taken after exposing the sample showing the spectrum of Fig. 2a to γ-rays of 2×10^6R or after heating it at 1150° C for 6 h in a nitrogen atmosphere. The figure shows that the original spectrum was converted into a broadened singlet by each of the two treatments. In contrast to this, no appreciable change was brought about on the spectrum of Fig. 2b by the same exposure, as demonstrated in Fig. 6b. For an exposure of 4.2×10^6 R, however, the spectrum turned into a broadened singlet of Fig. 6c, which is possibly the same as that of Fig. 6a. A similar change was observed to occur for the same spectrum only when the sample was quenched to room temperature, after annealing at 1150° C for 5 h in a nitrogen atmosphere. This singlet intensity gradually decreased while the sample was kept at room temperature, as illustra-

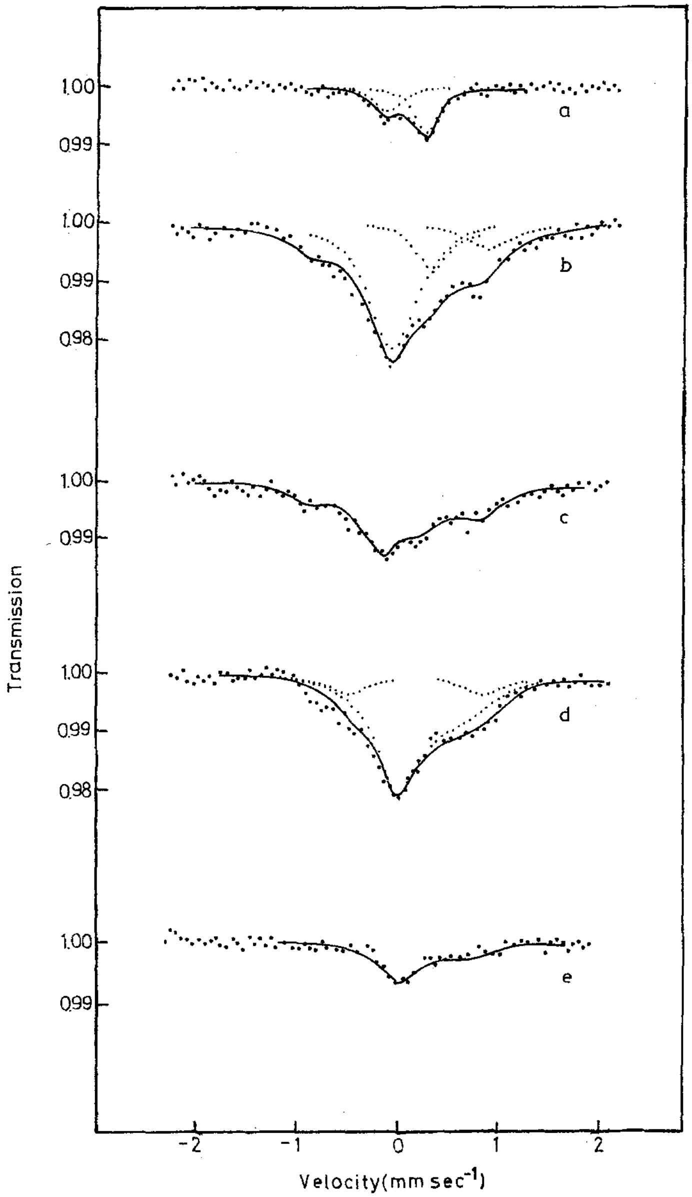

Figure 2 Variation of the spectrum of Fig. 1a by the following treatments: (a) annealing at 600°C for 1 h in air, (b) subsequent doping with ^{57}Fe, (c) and (d) further storage for 91 days and 493 days respectively at room temperature, and (e) treatment (a) followed by storage for 475 days at room temperature.

ted in Fig. 6d for storage of 61 days. Although the sample was further exposed to γ-rays of 1.4×10^6R, this spectrum was no longer varied.

In Figs. 7a and b show the Mössbauer spectra of β-silicon nitride doped with ^{57}Fe of 2.08 wt% measured after it was exposed to γ-rays of 4.85×10^6 R and 5.05×10^6 R, respectively. This substance was prepared from metallic iron, being mixed with a small amount of α-type. The marked change in question is obviously recognized to occur between the two spectra. Fig. 7c shows the Mössbauer spectrum of the same substance doped with natural iron of 14.38 wt%, indicating the presence of the singlet. It is to be noticed that on this spectrum weak hyperfine patterns due to iron in α-silicon nitride are superimposed as a background.

4. Discussion

The spectra of Figs. 1a and 2b, respectively, have three peaks at the central portion, apart from lines due to iron, which is only mixed with the samples. According to previous work [1] the central peak is ascribed to isolated Fe^{3+} ions substituted for silicon atoms, and the two remaining peaks are quadrupole doublet-pair of lines due to Fe^{3+} ions which are bonded to each other at two neighbouring silicon sites by a super-exchange force acting

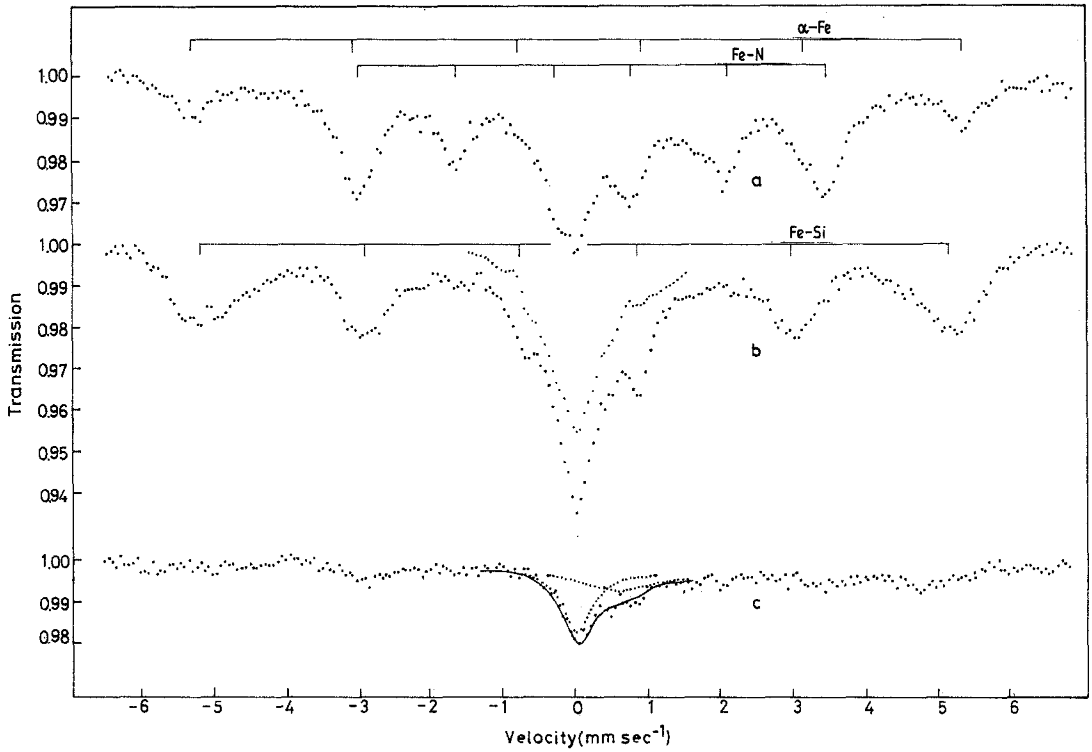

Figure 3 Variation of the spectrum of Fig. 2e by the following treatments: (a) doping with ^{57}Fe, (b) subsequent heating at 870° C for 20 h in a nitrogen atmosphere, and (c) further washing with the HCl solution.

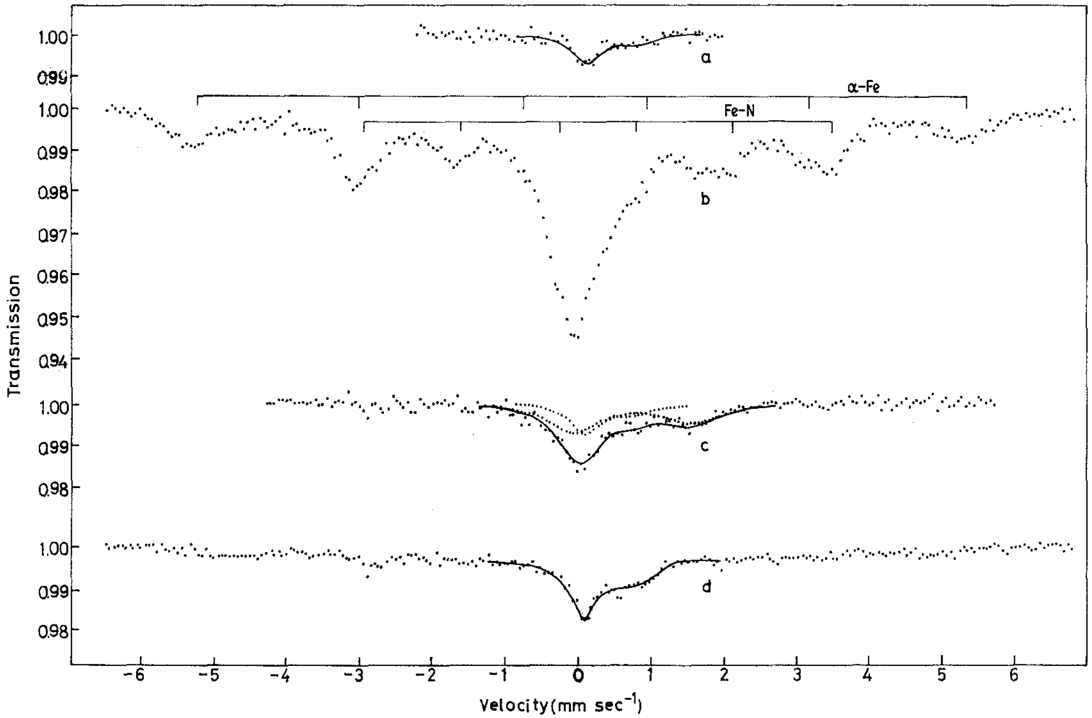

Figure 4 Variation of the uppermost spectrum (a), which is identical to that of Fi. 2e, by the following treatments: (b) doping with ^{57}Fe, (c) subsequent washing with the HCl solution, and (d) further heating at 1150° C for 8 h in an argon atmosphere.

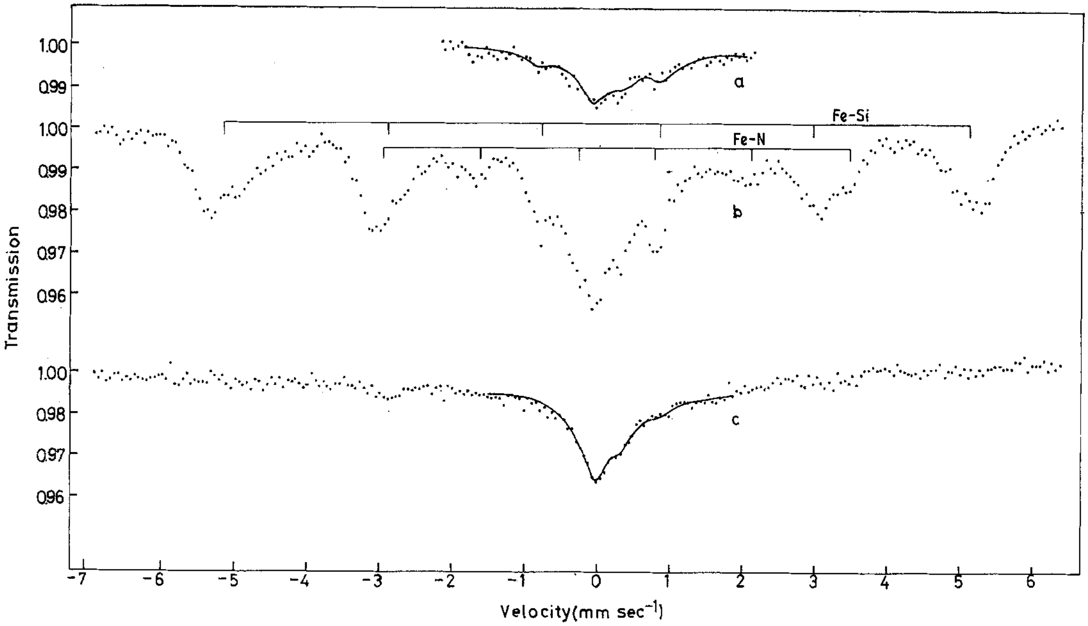

Figure 5 Variation of the uppermost spectrum (a), which is identical to that of Fig. 2d, by the following treatments: (b) doping with ^{57}Fe in a nitrogen atmosphere, and (c) subsequent washing with the HCl solution.

between them through an intervening nitrogen atom. However, it has not been attempted to resolve the three peaks into the respective components. Virtually, this resolution can be done well with each component shape being Lorentzian, as represented by separated dotted curves in Fig. 2b, and by a synthesized dotted curve in Fig. 1a. The figures indicate that the doublet is stronger in intensity than the singlet, and that it has an asymmetry which is too large to be attributed to the Godanskii–Karyagin effect or instrumental effects such as finite absorber thickness. These facts can be explained satisfactorily on the basis of the above model, provided that the exchange force is considerably stronger than the electronic repulsive force between the two ions. The large asymmetry is, of course, attributed to electronic relaxation of the linked spins of the two ions through spin-lattice interactions.

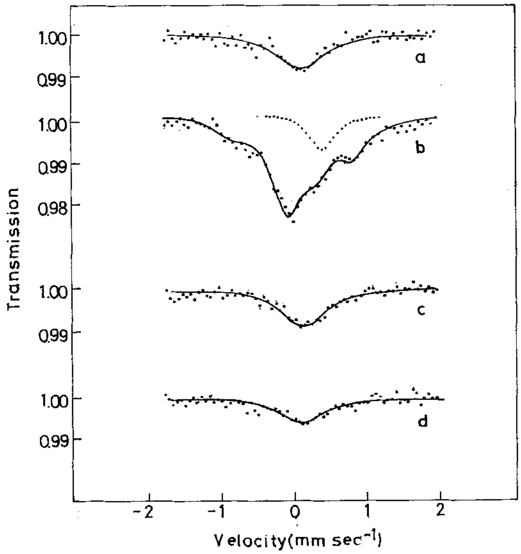

Figure 6 Variation of the spectrum of Fig. 2a by heating at 1150° C for 6 h in a nitrogen atmosphere or irradiation with γ-rays of 2×10^6 R. Variation of the spectrum of Fig. 2b by irradiation with γ-rays of (b) 2×10^6 R and (c) 4.2×10^6 R respectively, and (d) subsequent storage for 61 days at room temperature.

At first sight, the spectrum of Fig. 1b appears to consist of the three lines alone, apart from the two outermost lines arising from Fe_2O_3. Actually, their positions agree with those of the three lines of Fig. 1a, but inspection of the figure shows that the highest energy line is the only one that grows especially as compared with the others. To clarify the origin, we tried to resolve the spectrum into the three lines of Fig. 1a and other lines, assuming each line shape to be Lorentzian and using the synthesized curve of Fig. 1a. As a result, it was found that the resolution can be made satisfactorily enough provided that there is a distinct singlet just superimposed on the highest energy line, as indicated by a dotted curve. This new line gives an

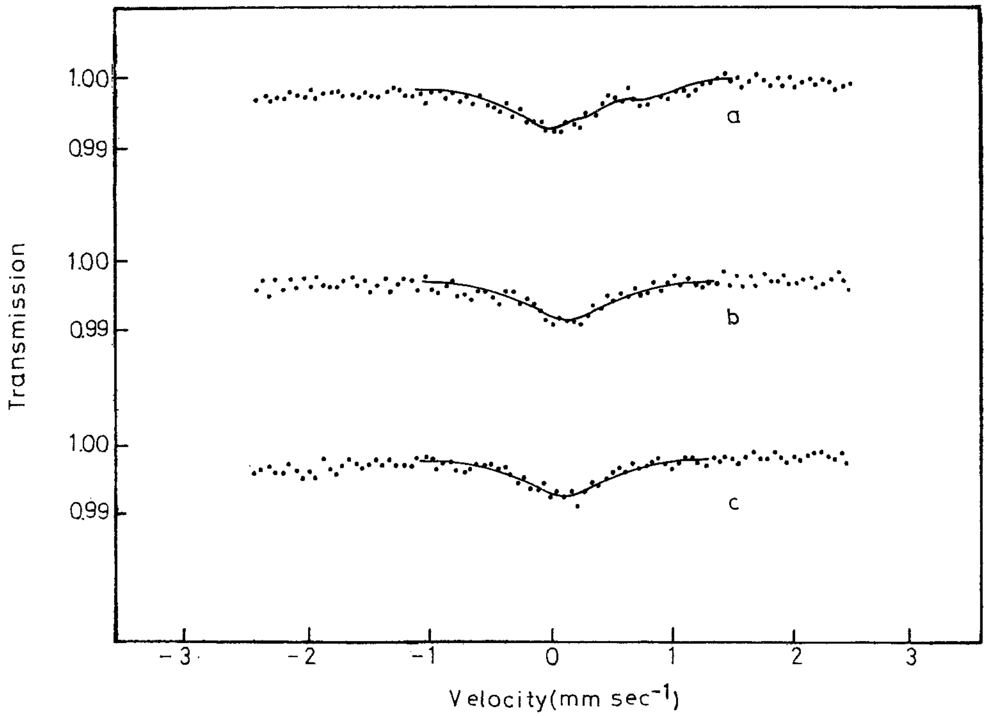

Figure 7 Mössbauer spectra of β-silicon nitride, prepared from metallic iron, which was lightly doped with ^{57}Fe and then exposed to γ-rays of (a) 4.85 × 10^6 R, and (b) 5.05 × 10^6 R respectively, and (c) which was heavily doped with natural iron.

isomer shift of 0.87 mm sec^{-1}, with a line width equal to that of the singlet of Fig. 1a. This singlet is interpreted as being ascribed to Fe^{2+} ions which were produced by reduction of the isolated Fe^{3+} ions caused by the residual carbon in the process of the doping.

Comparison of Fig. 1a and 2a reveals that the spectrum of the original sample changes greatly by annealing at 600° C for 1 h in air. The spectrum of Fig. 2a can be resolved well into two Lorentzian components with equal line widths, as shown by the dotted curves. It is obviously a quadrupole doublet, which gives an average isomer shift of 0.084 mm sec^{-1} and a splitting of 0.39 mm sec^{-1}. Since, as previously mentioned, the doublet is still observed even after storage of 438 days at room temperature, Fe^{3+} ions responsible for it are more stable than the isolated Fe^{3+} ions, by bonding to some defects. On annealing the sample in air, the residual carbon atoms escape as carbon oxides from the crystal leaving vacancies behind them. Actually, the presence of a considerable amount of silicon vacancies in such a sample was verified from the fact that ^{57}Fe can easily be doped to it, as compared with β-silicon nitride prepared from metallic silicon. Then, it is reasonable to consider that the Fe^{3+} ions in question accompany a respective silicon vacancy as the second nearest neighbour.

Figs. 2d, 2e, 3c and 4d show that all the spectra possess two peaks in the central portion. Any of the sets of the two peaks can equally well be resolved into two Lorentzian components having different line widths and almost equal areas, as illustrated by the dotted curves in Fig. 3c. They are a quadrupole doublet-pair of lines with an asymmetry caused by electronic relaxation, giving an average isomer shift of 0.35 mm sec^{-1} and a splitting of 0.65 mm sec^{-1}. From the fact that its ageing was no longer found at room temperature (after further keeping this sample for 887 days at room temperature, this spectrum was found to turn into that of Fig. 2d. This, together with the result for α-silicon nitride will be published in the near future [2]), species responsible for this doublet may be a precipitate iron or Fe–Si alloy or Fe–N alloy in the interstices. The Mössbauer spectra of $FeSi_x$ [3–12] and FeN_x [13–20] have been reported by many investigators for various values of x and several particle sizes, but all of them are in fair disagreement with the doublet under consideration. The species appear to be ascribed to iron clusters. Moreover, the weak extra lines of Fig. 2d may come from haematite fine particles.

The spectrum of Fig. 4c can be resolved well into the spectrum of Fig. 4a and two other components with equal line widths and Lorentzian shapes, as reproduced by the dotted curves in the figure. These two components are a quadrupole doublet-pair of lines, giving an average isomer shift of 0.75 mm $\sec^{-1}$ and a splitting of 1.6 mm $\sec^{-1}$. The line width of the components is greatly broadened to be 1.1 mm $\sec^{-1}$. This line broadening is clearly not due to thermal diffusion, electronic relaxation, and instrumental effects. It is attributed to a distribution of the environments of Fe^{3+} ions responsible for the doublet. Since the doublet intensity decreases gradually while the sample was stored at room temperature, the ions are known to be at substitutional sites. From the much later description, it is obvious that the doublet is not connected with interstitial Fe^{3+} ions other than the iron clusters. As previously stated, the spectrum of Fig. 4c or the doublet of interest is converted into the doublet due to the iron clusters when the sample is heated in a nitrogen atmosphere, but it shows no changes when the heating is made in an argon atmosphere. Consequently, the above conversion may be interpreted on the basis of assumptions that the Fe^{3+} ions are substituted for silicon atoms in the close vicinity of the iron clusters, by interactions with dipole moments created by a distortion of the atomic arrangement around them, and that nitrogen vacancies are formed at sites adjacent to these ions owing to weak bonding with their nearest neighbours. The reason is that those vacancies make it possible for the ions to transfer to the interstitial sites and to be bound to the clusters. If the above assumptions are thus accepted, the Fe^{3+} ions respectively yield doublets which are eventually smeared out to the observed broadened doublet.

As mentioned earlier, the doublet of Fig. 2a alters to the broadened singlet of Fig. 6a either by irradiating with γ-rays or by heating, and so do the three lines of Fig. 2b, as demonstrated in Fig. 6c. Comparison between Figs. 7a and b suggests that this change is likely to occur suddenly at a certain value of exposure. This critical value seems to vary from sample to sample, depending on the number of free silicon vacancies. That is, the larger the latter, the smaller the former. Radiation effects have been studied on the properties of a large number of solids. As far as the authors' knowledge is concerned, however, such a marked phenomenon does not seem to have so far been reported. Figs. 7a and 7c indicate that the Mössbauer spectrum of β-silicon nitride includes the three lines when lightly doped with ^{57}Fe, while it includes the singlet alone when doped heavily with natural iron without additional treatments. These facts, together with the ageing as in Fig. 6d, lead us to the conclusion that the singlet arises from substitutional Fe^{3+} ion clusters with appreciable sizes. The clusters are formed by the superexchange interaction already described, with an energy superior to the sum of energies of the strain field around the ions and the electrostatic repulsive interaction among them. Obviously, the line broadening is due neither to thermal diffusion nor to instrumental effects such as finite absorber thickness. It is interpreted as being due to relaxation of the resultant electronic spin of the ions through spin-lattice interactions.

Subsequently, let us discuss the origin of the marked change of the spectra caused by γ-irradiation. The spectra of Figs. 2a and 6a display their areas to be approximately equal to each other. Also, Figs. 7a and b shows that there is only a little difference between the areas of the portions in question of the spectra. In contrast to these, a much larger difference is seen between the areas of the spectra of Figs. 2b and 6c. Since a recoilless fraction does not seem very different before and after the sudden change, the above facts imply that the substitutional Fe^{3+} ions are displaced partly to the interstitial positions by interactions with γ-rays above the critical exposure, and that the number of the displaced ions is likely to depend strongly on the number of ions which are initially present at the substitutional sites. It was described that the singlet is also yielded by the heat treatment alone. It is to be noted that this heat treatment does not produce additional silicon vacancies but enhances diffusion of the Fe^{3+} ions, because a thermal equilibrium is already established in the doping process at the same temperature. These descriptions suggest that the displacement of the Fe^{3+} ions is taking place in the process of the marked change, and that both phenomena are connected with enhanced diffusion of the Fe^{3+} ions by silicon vacancies newly generated by γ-rays.

In the previous paper, it has been described simply that the transferred ion oscillates in a potential energy curve possessing some equivalent

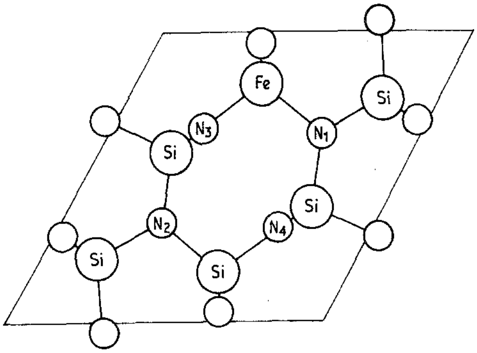

Figure 8 Projection of the unit cell on the c-plane in β-silicon nitride. Silicon and nitrogen atoms and the Fe^{3+} ion are denoted by Si, N and Fe respectively.

minima, without specifying a definite model. Here it is necessary to note that contrary to β-silicon nitride, the Mössbauer spectrum of α-silicon nitride reveals no ageing at room temperature, and also is not converted into the singlet by heating or irradiating with γ-rays [2]. The above model, therefore, must be specified on the basis of the difference between the crystal structures of the two substances [21, 22]. Fig. 8 exhibits the unit cell of β-silicon nitride [22], in which silicon and nitrogen atoms and the Fe^{3+} ion are, for simplicity, denoted as Si, N and Fe, respectively. A substitutional Fe transfers by a thermally activated process from its original site to an intermediate position between N_1 and another N atoms which is 0.29 nm distant from N_1 above and below along the c-axis and is covalently bonded to both N atoms by partly accepting their lone-pair electrons, each with the charge lobe directed towards the Fe. A similar situation is realizable at N_2. Owing to rearrangement of the electron configuration of N_1 after the Fe-transfer, the former position can be more stable than the latter. At the middle position between N_3 and N_4, the bonds among the Fe and these atoms may be thought to be very weak, since the lobes of their lone-pair electrons are 0.145 nm distant from each other along the c-axis, though they are directed towards the same direction. After the Fe-transfer, N_3 adjacent to the original site of the Fe like N_1 can change its electron configuration to accommodate the Fe at that position most favourably. Taking this fact into account, the Fe can be stabilized appreciably at that position. As a result, the potential energy curve for the Fe seems to be as schematically depicted in Fig. 9. Since the barriers separating the three minima would not be very high, the Fe positioned at one of them recoils to the other when it absorbs 14.4 KeV γ-rays. Thus the corresponding Mössbauer spectrum is not expected to be observed, which agrees with the experimental findings. If the Si atom adjacent to both N_2 and N_4 moves into the vacancy left behind by the transferred Fe while the latter is located above or below N_2, the resulting potential energy curve becomes identical to that of Fig. 9. Such a motion, which is enhanced by the weakened Si–N_2 bond, makes it possible for a silicon vacancy to diffuse, even at room temperature. A similar model is not accepted for α-silicon nitride because of the large distance between the two corresponding nitrogen atoms.

The interaction of β-silicon nitride with the γ-rays occurs principally by means of collisions with electrons produced by the Compton effect. According to theories developed by several workers [23–25], the number of the displaced Si atoms by elastic collisions with the Compton electrons is calculated to be negligibly small for exposure of

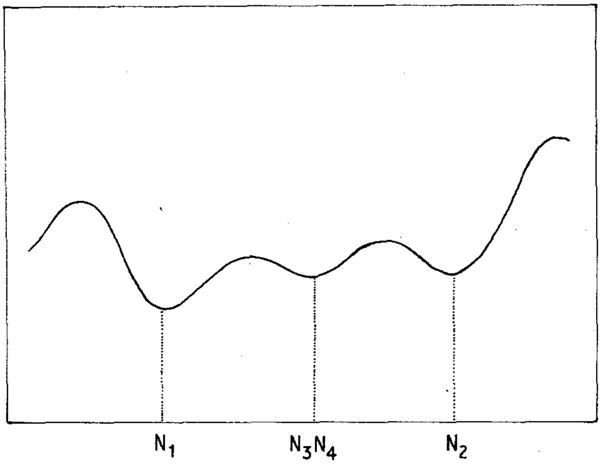

Figure 9 Schematic potential energy curve for an interstitial Fe or Si ion. N_1, N_2, N_3 and N_4 represent respectively the positions indicated by the same notations as in Fig. 8.

the order of 10^6R. Consequently, the displacement by inelastic collisions has to be considered for energy loss about 10^3 times larger than that due to the elastic collisions. Indeed, the radiation effects on the Mössbauer spectrum of α-silicon nitride is satisfactorily explained by these collisions [2]. Suppose that a silicon atom is positively charged by single or multiple ionization by the Compton electrons, and that before recombining with the ionized electrons, the resulting ion transfers to an intermediate position between two nitrogen atoms, as in the case of an Fe^{3+} ion. The transferred Si ion can move in a potential energy curve similar to that of Fig. 9. Then the vacancy left behind the ion is considered to move around on the crystal lattices in a similar way, resulting in radiation-enhanced diffusion of the Fe^{3+} ions at room temperature. It has been reported that the ageing of the three lines like Fig. 2c is greatly suppressed by high exposures like 1×10^7R. This fact is also readily explained on the basis of the above model, since the substitutional Fe^{3+} ions are disturbed by the presence of the displaced Si ions to transfer to the interstitial positions.

In the case that all the interstitial Si and Fe ions are very distant from one another, they move randomly and their movement produces no effect on the Mössbauer spectra. When the ions approach one another, their movement is limited by some special conditions. For example, if two of them happen to occupy simultaneously the positions above and below N_1 in Fig. 8, the potential energy curve at N_1 of Fig. 9 is fairly reduced, since these two ions are weakly bonded to the three nitrogen atoms compared with the case of the one interstitial. Such a configuration is, therefore, realized only with a very small probability. Suppose that the interstitials distributed over a limited region of the interstices are in a cooperative motion. Such a motion would set in only when the sum of the two kinds of the interstitials is beyond a certain value which is determined by factors such as the crystal structure and the cluster size. This movement makes it easy for the substitutional Fe^{3+} ions to diffuse by the above mechanism and to combine to form the clusters. The sudden change of interest may be understood to occur in this manner.

Finally, we will discuss the other lines seen in the spectra of Figs. 3a, 3b, 4b and 5b. The spectra of Figs. 3a and b display evidences of six-line patterns. From the similarity of the Mössbauer parameters, the six-line pattern denoted by Fe–N in Fig. 3a is identifiable to ϵ-nitride with nitrogen concentration slightly different from 27.3 at% [17]. The complex hyperfine pattern of Fig. 3b may be ascribed to a Fe–Si alloy, since its Mössbauer parameters are very close to those of a magnetic hyperfine pattern taken on Fe–Si alloy with a silicon concentration of 7.92 at%. In order to examine the cause of a strong broad peak which is located at each central portion of the spectra of Figs. 3a and b, we substract the doublet of Fig. 3c and the hyperfine pattern due to the Fe–Si alloy from the spectrum of Fig. 3b. A broad singlet then is found to be located at an isomer shift of $0.056\,\mathrm{mm\,sec^{-1}}$, as demonstrated by a dotted curve in the figure. This singlet is interpreted as arising from iron fine particles, which as well as the Fe–Si and Fe–N alloys are outside the crystal, since the singlet disappears by treatment with the HCl solution.

The spectrum of Fig. 3a has no trace of the hyperfine pattern due to the Fe–Si alloy, while the spectrum of Fig. 3b possesses no evidence of metallic iron and the Fe–N alloy. Comparison of Figs. 3a and 4b indicates that the two spectra are essentially identical with each other. The singlet arising from the iron fine particles is more intensified in Fig. 4b than in Fig. 3a, whereas the hyperfine pattern due to the Fe–N alloy reveals an opposite tendency. In Figs. 1b and 2b, the line due to metallic iron are seen, though not clear in the former, while the spectra due to the two alloys and the iron fine particles do not exist. These facts may suggest that the iron fine particles are formed by reduction of the Fe–N alloy. This conjecture however contradicts the spectrum of Fig. 5b. Comparing this spectrum with those of Figs. 3a and b, the hyperfine patterns of Fig. 5b are known to arise readily from the Fe–Si and Fe–N alloys. The hyperfine pattern due to the Fe–N alloy completely disappeared when the ^{57}Fe-doping was performed for a much longer period of time, not followed by the emergence of the spectrum arising from the iron fine particles. This contradiction is not yet cleared up. The central portion of Fig. 5c can be fitted well to the synthesized curve of Fig. 1a multiplied by a factor, as indicated by a solid curve. Traces of both the two doublets of Fig. 4c are not found, although a considerable amount of Fe^{3+} ions can be present there in the sample before doping.

It is interesting to note that although the ^{57}Fe-doping is performed under almost the same conditions, the different kinds of the species are pro-

TABLE I Relation between Mössbauer spectra of β-silicon nitride before ^{57}Fe-doping and species involving iron produced inside and outside the crystal after the doping. In the first row, the figure numbers showing the corresponding spectra are denoted.

Fig. 1a	Fig. 2a	Fig. 2c	Fig. 4a
Fe^{3+} (Si) Fe^{2+} (Si) α-iron (?)	Fe^{3+} (Si) α-iron	Fe^{3+} (fine particles) Fe–N alloy Iron fine particles α-iron	Fe^{3+} (Si) Fe–N alloy Fe–Si alloy α-iron (?)

duced inside and outside the crystal, depending on the state of iron which is present prior to doping, as summarized in Table I. It is worth noting that in the present experiment the Fe–N alloy was produced at a high temperature of 1150° C. This fact contrasts with usual preparation of Fe–N alloys which are undertaken at much lower temperatures. The reasons for these facts are not yet understood.

5. Conclusions

The results obtained by the previous and present studies are summarized as follows. Iron introduced in β-silicon nitride as an impurity and by thermal diffusion is equally substituted for Si atoms as for iron ion. The Fe ions are usually in the trivalent state, and exceptionally in the divalent state, and they occupy two neighbouring, as well as isolated silicon sites. At an elevated temperature, the isolated Fe ion combines with a silicon vacancy as the second nearest neighbour. It transfers from the substitutional site to the interstitial position, and then moves in the potential energy curve with the three non-equivalent minima, even at room temperature. This movement enhances the Fe ion and Si atom to diffuse over a wide region of the respective site at that temperature. Possibly, by this mechanism, a fraction of the Fe ions forms the clusters in the interstices. The ions also aggregate to form clusters at substitutional sites either by heating at a high temperature or by exposing to γ-rays. This aggregation in the irradiation process occurs suddenly at a certain value of exposure. This marked phenomenon may be explained in terms of a cooperative motion of all interstitial Si and Fe ions which sets in only on the sufficient approach of the ions to each other and enhances diffusion of the substitutional Fe ions to form the clusters. The Si ion is created as a result of the multiple ionization of the Si atoms immediately followed by transfer to the interstitial position, and it oscillates in the potential energy curve similar to that for the Fe ion. In the ^{57}Fe-doping process, the Fe–Si and Fe–N alloys and the iron fine particles are observed to form outside the crystal. The formation of these species is likely to depend on the state of the pre-existing iron inside the crystal.

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