Mössbauer Study of Iron in α - Si_3N_4 —Effects of Heat Treatment and γ -Irradiation

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The effects of heat treatment and γ -irradiation on the defect structure of α - Si_3N_4 doped with ^{57}Fe were studied by the Mössbauer effect. The complex spectrum observed is interpreted as consisting of two six-line patterns arising from isolated Fe^{3+} ions which are in high- and low-spin states respectively at two nonequivalent Si sites and of a quadrupole doublet arising from paired Fe^{3+} ions at two neighboring Si sites. The heat treatment of the sample in a nitrogen atmosphere intensified only the six-line pattern due to Fe^{3+} ions in the low-spin state and weakened the quadrupole doublet. γ -irradiation of 1.1×10^8 R yielded an intensity decrease of about 40% over the entire energy region of the spectrum, and an additional irradiation of 1.2×10^8 R brought about only a slight intensity increase of the quadrupole doublet. These results are very different from those for β - Si_3N_4 ¹⁾, which are interpreted on the basis of diffusion mechanisms of interstitial Fe and Si ions displaced from the substitutional sites. On the other hand, the heat treatment in air was found to force all the substitutional Fe^{3+} ions to form iron clusters and haematite fine particles in the interstices, and haematite fine particles and other unidentified species outside the crystal.

1 Introduction

In the application of Si_3N_4 to nuclear and industrial fields, it seems to be important to examine defects which are introduced into the crystal by heating at high temperatures or by highly exposing to radiations. As is widely known, Si_3N_4 has two modifications named α and β , and is usually prepared as a mixture of both types. Recently, we have undertaken detailed Mössbauer study of iron doped into β - Si_3N_4 to clarify the properties of defects introduced into it by the two treatments. As a result, a complicated change was observed to be caused on the Mössbauer spectrum, and shown to be explainable in terms of dynamics of Fe and Si ions as well as Si vacancy¹⁾. For these reasons, similar study is desirable to be carried out on α - Si_3N_4 . So, we examined the effects of both treatments on the Mössbauer spectrum of iron doped into this material, and obtained the results quite different from those for β - Si_3N_4 . This distinct difference in behavior of the two materials was interpreted as

originating from different mechanisms of interstitial Fe and Si ions displaced from the substitutional sites. Further, based on the above results, the state of the iron, *i.e.*, the properties of defects introduced were settled to some extent.

2 Experimental

The material used in this experiment was prepared by heating a 59.7% silica and 40.3% carbon mixture at 1520°C for 3 h in a flowing nitrogen (99.999% purity) and further by keeping the product obtained by the above procedure at 600°C for 1 h in air in order to remove residual carbon. The above mixture was produced by heating rice hull in the absence of air. In this process, most of other constituents of the hull such as organic compounds and water volatilized. The crystal structure of this material was verified with a X-ray diffraction method to be of α -type. ^{57}Fe was introduced into the crystal by thermal diffusion at 1150°C for 5 h in high-pure nitrogen sealed in quartz ampules. The Mössbauer spectra of the iron were measured with a $^{57}\text{Co}(\text{Cu})$ source at room temperature, their isomer shift being given with respect to metallic iron. In the case where it was necessary to remove lines arising from such

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extra species as metallic iron and haematite which were only mixed with the crystal or adsorbed on the crystal surface, the samples were washed in boiling 18% HCl solution for a prolonged period of time and then filtered. Such a treatment has been verified to be satisfactory enough for the above purpose. Exposure to radiation was made using γ -rays from a ^{60}Co source at room temperature.

3 Results and Discussion

In Fig. 1 are shown the Mössbauer spectra 1 and 2 measured on the two samples with the same thickness: one untreated, and the other annealed at 1150°C for 24 h in a nitrogen atmosphere and then quenched to room temperature. The figure reveals that such a heat treatment intensifies the lines denoted by arrows while it weakens the two lines located at the central portion. The remainings is not changed, as

presumed from the behavior of the highest and lowest energy lines on which, as described later, no other lines are superimposed. For the sample heat-treated at 1150°C for 8 h, an analogous intensity variation was found to occur with the magnitude equal to about one-third of that for 24 h. In each case, the areas of the intensity-increased and -decreased portions are equal to each other within an experimental error.

The upper portion of Fig. 2 displays the Mössbauer spectra 1 and 2 of the same sample taken after and before exposure to γ -rays of 1.1×10^8 R. The difference between the spectra 1 and 2 is depicted in the lower portion of the same figure. It is seen from the figures that the exposure causes an intensity decrease of about 40% over the entire energy region of the spectrum. An additional exposure of 1.2×10^8 R slightly intensified only the two central lines,

Fig. 1 Mössbauer spectra of $\alpha\text{-Si}_3\text{N}_4$, which was doped with ^{57}Fe and then treated with the HCl solution, taken (1) before and (2) after annealing in a nitrogen atmosphere at 1150°C for 24 h

Fig. 2 Mössbauer spectra of $\alpha\text{-Si}_3\text{N}_4$, which was doped with ^{57}Fe and then treated with the HCl solution, measured (1) before and after exposure to γ -rays of (2) 1.1×10^8 R and (3) 2.3×10^8 R respectively

as seen from the spectrum denoted by 3. Contrary to this, the remainings was not changed apparently, so that it is not plotted in the figure in order to avoid confusion. The above experimental results lead us to the conclusion that the Mössbauer spectrum of ^{57}Fe contained in $\alpha\text{-Si}_3\text{N}_4$ consists of two six-line patterns and a quadrupole doublet arising from different species, and that the species responsible for the doublet can be converted to only those for one of the two six-line patterns in the heat treatment.

The line positions of one of the two six-line patterns can be relatively readily settled from the intensity variation, as indicated by an upper set of six vertical lines in Fig. 1. These positions gives an internal magnetic field of 207 kOe, with a quadrupole splitting of 0.07 mm/s and an isomer shift of 0.43 mm/s. At first sight, the line positions of the other six-line pattern appears to be hardly settled, except for the highest and lowest energy lines. Inspection of the figure, however, makes it possible to settle the line positions. In the components of the six-line pattern already settled, the highest energy line is stronger in intensity than the lowest energy one, although the intensity change by the γ -irradiation seems to be approximately equal for both lines. One line in question should then be superimposed with this highest energy line. For the reason described later, the lower energy component of the quadrupole doublet must be thought to be considerably intensified owing to the overlapping with other lines, thereby one line having to be positioned at this energy. The six-line pattern settled in this way is indicated by a lower set of six vertical lines in Fig. 1. These line positions yield an internal magnetic field of 315 kOe, with a quadrupole splitting of 0.17 mm/s and an isomer shift of 0.17 mm/s.

In the previous paper²⁾, we have interpreted that the two six-line patterns respectively correspond to the $|\pm 5/2\rangle$ and $|\pm 3/2\rangle$ spin states of the ^6S electronic state of Fe^{3+} ions substituted for Si atoms, and that the apparent broadening of the highest and lowest energy lines are due to the overlapping of the two six-line patterns, with the slightly different parameters, arising from Fe^{3+} ions which are in $|\pm 5/2\rangle$ spin state

but at two nonequivalent Si sites in the unit cell³⁾. From Fig. 1, however, such an interpretation is evidently unacceptable for the six-line pattern associated with the internal field of 207 kOe. The magnitudes of the internal field lead us to the conclusion that the two six-line patterns arise from Fe^{3+} ions which are substituted for the two nonequivalent Si atoms in the unit cell and are correspondingly in the high- and low-spin states. This identification is also compatible with the fact that a Fe^{3+} ion located at one of the two Si sites is, as seen from Fig. 1, much more stable than at the other, indicating the stronger crystalline field at the former than at the latter site. The values of the internal field smaller and larger than those expected from the Fermi contact contribution of 550 and 110 kOe for the respective spin states of a $3d^5$ configuration originate mainly from a great amount of charge transfer between the Fe^{3+} ion and four nitrogen neighbors, as also inferred from the values of the isomer shift. Besides this, covalency in chemical bonds formed between them also contributes to the above deviation, and so does the distortion, though slight, of the environments around the ions from a regular tetrahedron. The spectroscopic terms of free Fe^{3+} ions in the high- and low-spin states are ^6S and ^2D , respectively. Virtually, the angular momenta of these ions in the crystal fairly deviate by the charge transfer from 0 and 2. As a result, it is conceivable that the six-line pattern arising from the Fe^{3+} ions in the high-spin state is greatly broadened by electronic relaxation as compared with the other.

The quadrupole doublet gives an average isomer shift of 0.56 mm/s and a splitting of 0.78 mm/s. These values respectively are comparable to 0.47 and 0.83 mm/s, the corresponding values of the quadrupole doublet of $\beta\text{-Si}_3\text{N}_4$. This fact allows us to interpret the quadrupole doublet in question as coming from paired Fe^{3+} ions substituted for two neighboring Si atoms, as in $\beta\text{-Si}_3\text{N}_4$.

The Mössbauer spectra revealed by $\alpha\text{-Si}_3\text{N}_4$ in the heat treatment and γ -irradiation are very different from those by $\beta\text{-Si}_3\text{N}_4$. As seen in Fig. 1, the doublet of $\alpha\text{-Si}_3\text{N}_4$ is only partly converted to the six-line pattern associated with the internal field of 207 kOe when heated at

1150°C for 24 h. In β - Si_3N_4 , the doublet together with the singlet due to the isolated Fe^{3+} ions is converted completely to a distinct broadened singlet even by heating for a shorter period of time at 1150°C. Such a conversion is also observed to occur by irradiating with γ -rays of pertinent exposure. Further, all the Mössbauer lines of β - Si_3N_4 gradually decrease in intensity upon keeping at room temperature, while such an aging is not found to occur in α - Si_3N_4 even by storing for a much longer period of time. Contrary to β - Si_3N_4 ¹⁾, α - Si_3N_4 has no interstitial site at which a displaced Fe or Si ion becomes stable by bonding with its surroundings, and consequently the ions move around the interstices readily and randomly, as inferred from the fact that the displaced Fe ions exhibit no Mössbauer lines. This matter implies that in contrast with β - Si_3N_4 , in α - Si_3N_4 these ions annihilate relatively easily by recombining with Si vacancies during each treatment and do not take place a cooperative motion, accompanied by enhanced diffusion of Si vacancies, under any conditions¹⁾. Further, owing to the strong bonding with the nitrogen neighbors, in α - Si_3N_4 the central Fe^{3+} ions are hard to be displaced, through a thermally activated process, at room temperature. For these reasons, the two materials display the different behavior as described above.

It was already pointed out that after the initial exposure to γ -rays of 1.1×10^8 R, the Mössbauer spectrum shows the intensity decrease of about 40% over the entire energy region, without accompanying the appearance of any new lines. This fact leads us to the conclusion that the substitutional Fe^{3+} ions are equally displaced by γ -rays to the interstitial positions, regardless of the sites occupied by them. The probability that the two neighboring Fe^{3+} ions are simultaneously displaced directly by γ -irradiation is extremely small, compared with the isolated Fe^{3+} ions. Consequently, it is suggested that as for the paired Fe^{3+} ions, the displacement of one constituent ion is necessarily followed by the simultaneous displacement of the other, probably owing to a superexchange force acting between the two ions through an intervening nitrogen atom on which two electrons with antiparallel spins reside. It is obvious that under

the above exposure, the displacement process is superior to the annihilation process. The non-appearance of any lines associated with the displaced Fe^{3+} ions is due to the fact that the ions easily recoil when absorb 14.4 keV γ -rays, as already mentioned. It was further stated that for the additional exposure of 1.2×10^8 R the doublet is intensified but all the other lines remain unaltered. This experimental fact reveals that for the paired sites the annihilation process is superior to the reverse process, while for the isolated sites an equilibrium is established between the two processes. Combining with the foregoing result, the kinetics of the displacement process is considerably complex for the paired Fe^{3+} ions.

The displacement is taken place by elastic and inelastic collisions principally with Compton electrons of the material with γ -rays. According to theoretical treatments developed by several workers⁴⁻⁶⁾, the fraction of the displaced ions by the elastic collision is found by calculation to be of the order of 10^{-5} . This value is quite negligibly small. In the above calculation, 1 eV was used as a displacement threshold energy, which is approximately equal to an energy required to displace a substitutional Fe^{3+} ion in β - Si_3N_4 ²⁾. So, let us take into account the displacement by the inelastic collision. If one Fe^{3+} ion is displaced in each event, the fraction of the order of 1% is obtained by simple calculation. The fairly good agreement between the calculated and experimental values may be rather fortuitous, since the calculation was made with rough approximations. For instance, the following facts have to be taken into consideration: (1) the actual threshold energy is a little larger than 1 eV as stated earlier, and (2) the partial annihilation of the displaced Fe^{3+} ions occurs during the irradiation. However, the above result explicitly indicates that the inelastic collision plays a dominant role in displacing the substitutionals. Moreover, the heat treatment brings about no displacement of the Fe^{3+} ions, as seen in Fig. 1. The reason for this is that prior to this treatment, a thermal equilibrium is already established between the substitutionals and interstitials during the doping process.

Finally, we will describe changes of the

Fig. 3 Mössbauer spectra of α - Si_3N_4 , which was doped with ^{57}Fe and then treated with the HCl solution, recorded (a) after heating in air at 1150°C for 5 h and (b) after subsequently treating with the HCl solution

Mössbauer spectrum when the sample was heated in air at 1150°C for 5 h. Fig. 3 (a) displays the Mössbauer spectrum observed after the sample showing the spectrum 1 of Fig. 1 was treated in this way. The figure reveals that the complex hyperfine patterns are replaced by two strong lines positioned at the central portion and by additional weak lines, which arise evidently from metallic iron, appearing on their both sides. When this sample was further treated with the HCl solution, we obtained the Mössbauer spectrum of Fig. 3 (b), in which a distinct hyperfine pattern appears at the central portion. Since the weak lines due to metallic iron are not seen in this spectrum, the iron is known to be outside the crystal. Subtracting the spectrum of Fig. 3 (b) from that of Fig. 3 (a), obviously a spectrum with two strong peaks is obtained (not shown in the figure). This spectrum can be decomposed into strong and weak paired components, as indicated by dotted curves in Fig. 3 (a). The former components are quadrupole doublet-pair of lines, giving an average isomer shift of 0.28 mm/s and a splitting of 1.1 mm/s . This doublet is quite different from anyone of the spectra, reported by other workers, arising from fine particles of Fe-N and Fe-Si alloys⁷⁾ and metallic iron⁸⁾. A similar quadrupole doublet is displayed on the Mössbauer spectrum of an amorphous ultra-thin film of Fe_2O_3 on graphite, having the isomer shift of 0.35 mm/s and the splitting of 0.95 mm/s which are close to the above corresponding values⁹⁾. Since these para-

meters are dependent of the film or particle size, the doublet in question seems to be attributed to haematite fine particles outside the crystal. A quadrupole doublet consisting of the latter components yields an average isomer shift of 0.31 mm/s and a splitting of 1.9 mm/s . This doublet has too large splitting to be identified to haematite or iron particles. Species giving rise to it, which is also outside the crystal, is hardly settled at the present.

In order to clarify the origin of the hyperfine pattern of Fig. 3 (b), we measured the Mössbauer spectrum of β - Si_3N_4 heat-treated in a similar way, since a variety of the spectra shown by this material in several treatments appears to have been identified¹⁾. In Figs. 4 (a) and (b) are respectively indicated the spectra before and after such a heat treatment. The material, prior to this heat treatment, was doped with ^{57}Fe , then stored for 887 days at room temperature and finally treated with the HCl solution. The above two spectra are seen to be identical to each other, apart from a very weak six-line pattern due to haematite formed inside the crystal. The hyperfine pattern can well be decomposed into two quadrupole doublets, as indicated by dotted curves. One of them, which is depicted by a synthesized curve, is attributed to iron clusters in the interstitial sites¹⁾. The other gives an average isomer shift of 0.22 mm/s and a splitting of 0.95 mm/s . For the foregoing reason, this doublet may be interpreted as coming from haematite fine particles formed inside the crystal. Since the hyperfine pattern of Fig.

Fig. 4 Mössbauer spectra of β - Si_3N_4 , which was doped with ^{57}Fe and then stored for 887 days at room temperature and further treated with the HCl solution, taken (a) before and (b) after heating in air at 1150°C for 5 h

3 (b) resembles in shape to that of Fig. 4 (a), it can be expected to be decomposed into components in a similar way. Actually, this decomposition can be made satisfactorily provided that there exist the quadrupole doublet due to the iron clusters and another quadrupole doublet, as indicated by dotted curve in Fig. 3 (b). The unspecified quadrupole doublet gives an average isomer shift of 0.11 mm/s and a splitting of 1.2 mm/s , and it may also be interpreted as being due to haematite fine particles.

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電気化学工業と電力貯蔵方式・調査報告書

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☆本報告書は、エネルギー問題の重要性に鑑み、電気化学工業において多面的に省資源・省エネルギー対応を図ると共に、電気事業にとっても極めて有効な方策の一つとして共通な課題である電力貯蔵方式について行った調査報告書です。

☆内 容 ○電気事業の現状 ○電気化学工業の現状 ○二次電池による電力貯蔵 ○電力貯蔵用新型常温電池 ○燃料電池による発電 ○水電解—燃料電池の組合せによる電力貯蔵 ○総括

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