Mössbauer effect of ^{57}Fe-doped silicon nitride

Silicon nitride has a great potential for high-temperature materials [1]. It has been well known that iron doping into silicon accelerates the nitridation of the material [2, 3]. The purpose of the present study was to clarify the role of iron in silicon nitride structure by means of iron-57 Mössbauer spectroscopy.

Silicon powder (99.999%) and a small amount of Fe_2O_3 (enriched with 94% ^{57}Fe) were mixed and pressed to pellets. They were put on dummy Si_3N_4 pellets to avoid direct contact with an Al_2O_3 boat, and were nitrided at a maximum temperature of 1430° C in a nitrogen gas atmosphere ($O_2 < 0.5$ ppm, dew point $< -60°$ C). The products were identified with an X-ray diffractometor as α–Si_3N_4 containing a small amount of β-Si_3N_4 and were subsequently studied by Mössbauer spectroscopy.

The Mössbauer equipment (Elscient Co) was used in a constant acceleration mode. The Mössbauer spectra were recorded at room temperature using a source of ^{57}Co in Cu, and the velocity scale was calibrated by an iron foil and sodium nitroprusside.

Fig. 1 shows a typical Mössbauer spectrum of 0.41 at.% Fe-doped silicon nitride. The spectrum is composed of two peaks of an equal intensity. The isomer shift (δ) was +0.277 mm sec^{-1}, indicating that the iron atoms were in the Fe^{3+} state [4]. The quadrupole splitting (ΔE_Q) was 0.531 mm sec^{-1}; Fe^{3+} is S-state ($3d^5$; $^6S_{5/2}$) and has no electric field gradient of its own. Thus, this relatively large value of ΔE_Q can come from a highly asymmetrical electrical environment around Fe^{3+} ions. A line width was 0.389 mm sec^{-1}, which was larger than that of sodium nitroprusside (0.248 mm sec^{-1}). Similar spectra were observed in the materials with dopant levels up to 0.63 at. % Fe and their Mössbauer parameters were independent of the Fe content. Above 0.63 at.% Fe, another magnetic hyperfine splitting appeared (Fig. 2). The magnetic hyperfine field and the peak positions agreed with those of metallic iron. A solubility limit of iron into Si_3N_4, therefore, would lie around 0.6 at. % at 1430° C.

In order to understand the magnitude of the quadrupole splitting observed, the observed ΔE_Q value was compared with the calculated one. The electric field gradient (eq), the asymmetry parameter (η) and the ΔE_Q can be given by the well-known relations [5]

$$eq = V_{zz}$$

$$\eta = |V_{xx} - V_{yy}|V_{zz}$$

$$\Delta E_Q = \frac{1}{2}e^2q'Q(1 + \frac{1}{3}\eta^2)^{1/2},$$

where e is the anion charge, diagonal elements (V_{ii}) are chosen so that $|V_{xx}| \leqslant |V_{yy}| \leqslant |V_{zz}|$, $q' =$

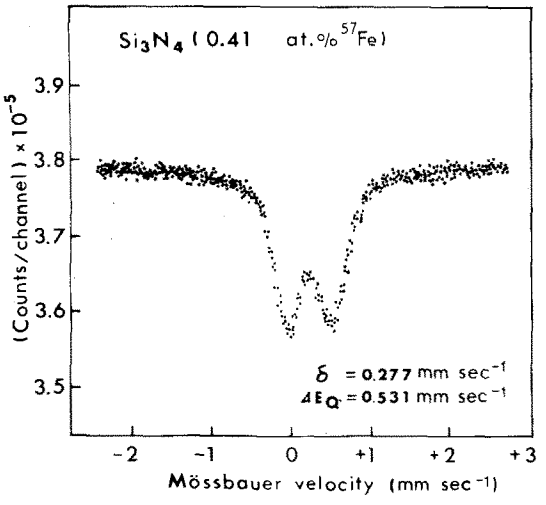

Figure 2 Mössbauer spectrum of 2.61 at. % ^{57}Fe -doped Si_3N_4 at room temperature.

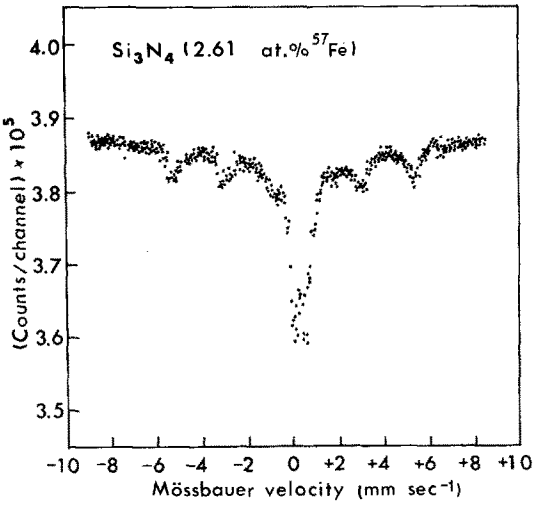

Figure 1 Mössbauer spectrum of 0.41 at. % ^{57}Fe -doped Si_3N_4 at room temperature.

TABLE I Calculations of the quadrupole splitting for Fe-doped Si_3N_4 containing nitrogen vacancies

Vacant site around Si (1)	$q \times 10^{-24}$ (cm^{-3})	η	ΔE_Q (mm sec^{-1}) ionicity		Vacant site around Si (2)	$q \times 10^{-24}$ (cm^{-3})	η	ΔE_Q (mm sec^{-1}) ionicity	
			30%	20%				30%	20%
N (1)	0.378	0.417	0.770	0.513	N (1)	0.420	0.104	0.833	0.555
N (1′)	0.324	0.347	0.655	0.436	N (2)	0.416	0.132	0.826	0.551
N (2)	0.422	0.056	0.834	0.557	N (2′)	0.347	0.559	0.721	0.481
N (3)	0.378	0.217	0.754	0.534	N (4)	0.369	0.288	0.740	0.493
		av.	0.765	0.502			av.	0.780	0.520

$(1-\gamma_\infty)\,q$, Q is the quadrupole moment of the first exited state of ^{57}Fe, and γ_∞ is the Sternheimer antishielding factor. The generally accepted values of γ_∞ and Q are -9.14 [6] and 0.20 barn [7], respectively.

The crystal structure of α–Si_3N_4 has been determined by X-ray diffraction, the space group being P31c [8]. There are two types of silicon positions Si(1) and Si(2), each of which is tetrahedrally surrounded by nitrogen atoms. It is assumed that silicon is replaced by iron in both sites, and that the degree of ionicity in Si_3N_4 is 30% according to Pauling's formulation [9]. The calculated values of ΔE_Q were 0.19 mm sec^{-1} for Si(1) site and 0.12 mm sec^{-1} for Si(2), when tetrahedron was fully occupied by nitrogen. Both values are much smaller than the observed one, 0.531 mm sec^{-1}. Further calculations were made by introducing a nitrogen vacancy in the tetrahedron, which may result to maintain charge neutrality over the whole volume. The calculated mean ΔE_Q for the silicon nitride containing the defects were 0.765 mm sec^{-1} for Si(1) site and 0.780 mm sec^{-1} for Si(2) site (Table I). These values are in approximate agreement with the observed one. On the other hand, the calculation for 20% ionicity showed $\Delta E_Q = 0.502$ and 0.520 for Si(1) and Si(2) sites, respectively.

It may be concluded, therefore, that the relatively large ΔE_Q observed in Fe-doped Si_3N_4 can be explained by the presence of a nitrogen vacancy. This conclusion may also supported by a study of nitrogen self-diffusion for "pure" and Fe-doped silicon nitride [10].

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