Nitridation of Silicon Powder

By

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1. Introduction

Nitridation process of highly pure silicon powder was reported to follow linear kinetics^{1),2)}, and the rate determining step was considered to be diffusion process of nitrogen atom through nitrided surface skin built on silicon particles^{2),3)}. From the linear kinetics, those nitride skin was considered to repeat cracking and exfoliation during the reaction^{2),3)}. The reaction rate was roughly proportional to the square root of particle diameter of silicon²⁾. The cause of the size effect, however, was left uncertain. A purpose of this report is to discuss the reaction process referring to the microstructure of reaction products.

2. Experiments

Highly pure and fine powder of silicon (average grain size; ca. $2\mu\text{m}$, purity $>99.999\%$) and commercially pure nitrogen ($\text{O}_2 < 0.5\text{ ppm}$, dew point $< -60^\circ\text{C}$) were used as reactants. Electron micro-

graphs of the raw silicon powder are shown in Fig. 1. One gram of silicon powder was moisten with distilled water and pressed in to a disk, 15 mm in diameter and ca. 4 mm in thickness. Average porosity of the pressed disks was ca. 39~40%. They were nitrided in a tubular furnace at 1220° , 1270° and 1410°C for about 3 h in nitrogen stream of 1 atmospheric pressure.

Fractions of nitrided silicon were calculated from the weight increment, and they were ca. 10, 20 and 90%, respectively. Microstructure of the samples were studied with electron microscopes.

3. Results

Microstructures of fracture surface of the nitrided samples are shown in Fig. 2~4. In the sample nitrided at 1220°C , initial outline of raw silicon powder still remained and silicon grains were lightly covered with fluffy reaction products as shown in Fig. 2-(a). Very thin, 100~200 Å thick products

Fig. 1 Electron micrographs of raw silicon powder.

Fig. 2 Scanning electron micrographs of fracture surface. (a) nitrided at 1220°C up to 10%, (b) nitrided at 1270°C up to 20%, (c) nitrided at 1410°C up to 90%, and (d) recrystallized β - Si_3N_4 prepared by heating the sample similar to that shown in (c) at 1730°C for 8 h in N_2 .

were found around the grains (Fig. 3), and they showed that the reaction did not proceed uniformly on the grain surfaces.

Fig. 2-(b) shows the sample nitrided at 1270°C. More reaction products were found than Fig. 2-(a). Fig. 2-(c) shows the sample nitrided at 1410°C. In the sample, most part of raw silicon was nitrided and the fracture surface clearly differed from that in Fig. 2-(a) in appearance. Thin flakes were found with high magnification (Fig. 4).

X-ray diffraction study showed that they were consisted of α - Si_3N_4 , β - Si_3N_4 and residual silicon. The ratio β/α was ca. 15/85 and was nearly independent of nitriding temperature. The contents of

α - Si_3N_4 seemed to increase slightly with decreasing reaction temperature.

Fig. 2-(d) shows a fracture surface of β - Si_3N_4 sample prepared by heating at 1730°C for 8 hr in nitrogen gas of 1 atmospheric pressure³⁾. Many prismatic microcrystals of β - Si_3N_4 in the figure clearly indicated recrystallization⁶⁾.

4. Discussion

The results obtained in the earlier section seems to support the kinetics described in the introduction. They, however, are not sufficient to explain grain size effect first reported by Hüttinger¹⁾. Thompson and Pratt³⁾ considered that the nitridation proceeded

Fig. 3 Electron micrographs of powdered sample nitrided at 1220°C up to 10%. Wide dark zones correspond to silicon grain.

Fig. 4 Electron micrograph of powdered sample nitrided at 1410°C up to 90%.

through cracking or exfoliation of very thin, said tens of Å thick, nitride films built on the surface of silicon particles by diffusion of nitrogen through the nitride films already formed; cracking and exfoliation were the results of volume increase of silicon nitride caused by nitridation at the interface between silicon and surface nitride skin.

Assume that the crack formation of the skin has an important role in the nitridation. As pointed out by Griffith,⁷⁾ the tensile strength σ of a brittle material is controlled by the equation (1). Here r

is surface energy of the material, E is elastic modulus and c is the size of initial flaw from which catastrophic fracture initiates, and A is a dimensionless geometrical constant.

$$\sigma = A(\gamma \cdot E/c)^{1/2} \dots \dots \dots (1)$$

The following thermodynamical relations⁸⁾ are obtained by introducing surface enthalpy ΔH_{sv} , lattice spacing d of the nitride and the particle diameter D of silicon,

$$E \propto \Delta H_{sv}/d$$

$$\gamma \propto \Delta H_{sv}$$

By assuming that c is proportional to D , Eq. 1 is transformed into the following equation :

$$\sigma \propto \Delta H_{sv}/(d \cdot D)^{1/2}$$

As the lattice spacing d is approximately constant, the following relation is obtained :

$$\sigma \propto \Delta H_{sv}/(D)^{1/2} \dots \dots \dots (2)$$

If the thickness of the surface skin in which cracks extend is kept nearly constant²⁾ during the reaction, as the number of cracks formed in unit surface area is considered to be proportional to $1/\sigma$, total length of the cracks in unit surface area is proportional to $(D)^{1/2}$ at constant temperature. Thus the reported results on the grain size effect is explained.

The activation energy of the reaction, 156~158 kcal/mol^{1),2)} may correspond to that of diffusion process of nitrogen through the thin nitride skin. Because, the cracking or exfoliation are considered to be the results of the diffusion as stated earlier.

Clear difference in microstructure between Fig. 2-(c) and (d) suggest that the transformation $\alpha \rightarrow \beta$ might occur through recrystallization⁹⁾. In the case of reaction between solid silicon and nitrogen, α -Si₃N₄ seems to be produced first and gradually recrystallize into β -Si₃N₄ in prolonged reaction period. Mechanical strength of reaction sintered articles will be brought by the [recrystallization.

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シリコン粉末の窒化

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シリコン粉末と窒素との反応で得られた生成物を電子顕微鏡を用いて調べ、形態観察の結果を基に反応機構を考察した。反応の速度が、シリコン粒子径の平方根に比例する事実は、Griffith の考え方を引用して説明された。観察結果は、この反応の活性化エネルギー、156～

158 kcal/mol が、シリコン粒子表面に、反応により形成された窒化物皮膜中を窒素が拡散する際の障壁に相当するものであろうとする考え方を支持するようなものであった。

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Measurements of Dielectric Relaxation in Oxide Glasses by Means of the Absorption Current Method

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1. Introduction

So far it has been believed that there is no dielectric relaxation peak corresponding to the mixed alkali peak or the high temperature peak in the mechanical relaxation [1-4]. Recently, however, the distinct dielectric relaxation peak was observed in the mixed alkali glasses [5, 6], which show a remarkably small dielectric loss current compared with the conduction current. The present paper describes the application of the absorption current method based on Hamon-Nakajima's approximation [7, 8] to the measurement of the dielectric loss in oxide glasses exhibiting a very small dielectric loss current.

2. Estimation of ratios of dielectric loss current to conduction current

The dielectric loss current $J(\omega)$ and the conduction current J_0 are given by

$$J(\omega) = \omega \cdot \epsilon_0 \cdot \epsilon''(\omega) \cdot E \quad \dots\dots\dots (1)$$

$$J_0 = \sigma \cdot E \quad \dots\dots\dots (2)$$

where $\epsilon''(\omega)$ is the dielectric loss factor at angular frequency $\omega (= 2\pi f)$, E is the field intensity. Therefore, the ratio $J(\omega)/J_0$ is given

$$\frac{J(\omega)}{J_0} = \frac{\omega \cdot \epsilon_0 \cdot \epsilon''(\omega)}{\sigma} \quad \dots\dots\dots (3)$$

According to Cole-Cole [9], the dielectric loss factor $\epsilon''(\omega)$ is

$$\epsilon''(\omega) = \frac{\frac{1}{2} \Delta \epsilon \cdot \cos \frac{1}{2} \alpha \pi}{\cosh(1-\alpha)x + \sin \frac{1}{2} \alpha \pi} \quad \dots\dots\dots (4)$$

$$x = \ln \omega \tau = \ln \omega / \omega_m$$

where τ is the dielectric relaxation time, ω_m is the angular frequency at the relaxation peak and α is the parameter that shows the distribution of the dielectric relaxation time. Putting eq. (4) in (3) gives

$$\frac{J(\omega)}{J_0} = \frac{\omega \cdot \epsilon_0 \cdot \Delta \epsilon}{2\sigma} \frac{\cos \frac{1}{2} \alpha \pi}{\cosh(1-\alpha)x + \sin \frac{1}{2} \alpha \pi} \quad \dots\dots\dots (5)$$

On the other hand, we have found [5, 6] the quantitative correlation between the conduction and the dielectric relaxation given by eq. (6)

$$\sigma = p \cdot \epsilon_0 \cdot \Delta \epsilon \cdot 2\pi f_m \quad \dots\dots\dots (6)$$

There are three types of diffusion processes characterized by the different correlation factors p and which cause the conduction or the dielectric relaxation in different manners [5, 6].