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Effect of Fe and Al additions on nitridation of silicon

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The effect of Fe and Al on the nitridation of Si was investigated under controlled O_2 partial pressures in the range 1.2×10^{-12} to 1.2×10^{-15} atm at 1420° C. The volatilization of Si during nitridation is attributed to SiO gas formation. Addition of Fe promoted the nitridation to α phase at lower temperatures than the melting point of Si, whereas addition of Al increased the amount of β phase. The stabilization of the β structure is explained by Al_2O_3 formation and the dissolution of it in Si_3N_4 to form (Si, AL)$_3$ (N, O)$_4$ (sialon).

1. Introduction

Despite extensive work on the reaction of Si and N_2 to form Si_3N_4 [1–4], discrepancies in the reaction kinetics have been observed. The variability in results is attributed to the mean particle size, particle distribution and impurities in Si and the atmosphere. Attempts have been made to determine the effect of O_2 on the nitridation reaction [4, 5]. Messier *et al.* [4] showed that O_2 retards the nitridation reaction; Mitomo [5] recognized the same effect together with the acceleration of α formation by O_2.

On solid impurities, Messier and Wong [6] observed the catalytic acceleration of the nitridation reaction by the addition of Fe and attributed this to the formation of an Si–Fe melt. However, Lin [7] suggested that Fe reacted with O_2 and SiO to form FeO, lowered the effective O_2 partial pressure and accelerated the nitridation reaction of Si. Suzuki [8] was able to obtain each of the pure phase, α or β, by addition of solid catalysts.

Factors which control the nitridation kinetics are complicated by the fact that reactions are usually carried out under conditions where Si_3N_4 is thermodynamically unstable with respect to SiO_2 [5]. Thus, the kinetics of nitridation must be investigated under controlled O_2 partial pressures in the nitriding atmosphere.

This paper deals with the effect of Fe and Al additions on the nitridation of Si and the formation of α and β phases under controlled O_2 partial pressures in the range 1.2×10^{-12} to 1.2×10^{-15} atm at 1420° C.

2. Experimental

The silicon powder used (Chisso Ltd) was high purity (> 99.99%) and the particle size was $< 3\,\mu$m. The impurities were qualitatively determined by laser-microspectrochemical analysis as Al, Ni, Mg > Fe, Pb, and Zr. Electrolytic Fe and Al powders (Koso Chemical Ltd) were of high purity (> 99.99% disregarding O). The N_2 gas used had ~ 20 ppm O_2 and a dew point < –50° C. It was mixed with H_2 to the ratio $N_2/H_2 = 4$, and passed at a flow rate of 180 cm^3 min^{-1}. The O_2 partial pressure was controlled in the range 1.2×10^{-12} to 1.2×10^{-15} atm at 1420° C by controlling the H_2O pressure in the N_2–H_2–H_2O gas mixture.

About 300 mg of the powder mixture of Si and 1 wt% Fe or Al was pressed under $\sim 4.3 \times 10^3$ psi* in 12 mm diameter steel die. The compact was suspended with Mo wire in a vertical furnace with SiC heating element and lowered into reaction zone after the desired temperature was attained. The reaction tube was made of alumina. The presence of Mo and alumina may not affect

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*10^3 psi = 6.89 N mm^{-3}.

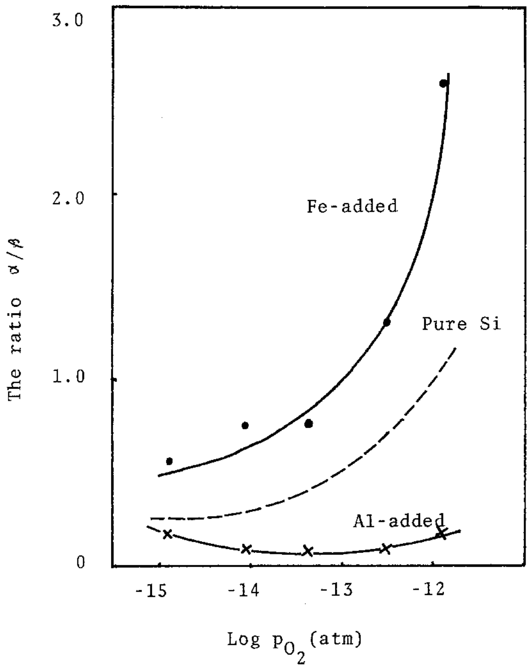

Figure 1 The dependence of the α/β ratio on O_2 partial pressure.

the O_2 pressure because H_2O pressures in $N_2-H_2-H_2O$ are large enough to be a buffer to maintain the constant O_2 pressure [9].

The compact was kept at 1350°C for 1h to nitride the surface in order to avoid melting the entire compact and then kept at 1420°C for 4h. It was then cooled and weighed. The crystalline composition was determined from a powdered sample using an X-ray diffractometer.

3. Results and discussions

The dependence of weight gain of the α and β phases on O_2 pressure in Si with added Fe and Al is shown in Table I. Increase in α and decrease in β with the increase of O_2 pressure in Fe-added Si is shown. In Al-added Si, however, the amounts of α and β phases are independent of O_2 pressure and Si is nitrided predominantly to β structure. The dependence of the ratio of α to β on O_2 pressure is plotted in Fig. 1 together with the results for pure Si at 1450° C [5].

After the low temperature (1350°C) heating for 1h, the amount of Si nitrided was about 10% in the Al-added system, giving equal amount of α and β. In the Fe-added system, about 40% Si was nitrided to give about 35% α and 5% β. This means that the higher α/β ratio in the Fe-added system compared with those for pure and Al-added Si (Fig. 1) is attributed to the acceleration of α formation at low temperature.

The decrease in the total amount of Si nitrided at the highest O_2 pressure (1.2×10^{-12} atm), even though the weight gain was large, shows that the nitridation of Si was retarded. This is consistent with X-ray analysis which showed the existence of Si_2ON_2 and a trace of cristobalite on the outermost layer of the compact.

The amount of residual Si determined by X-ray diffraction is always lower than that calculated from the weight gain and the voltalization of a certain amount of Si is expected. The amount of Si volatilized was calculated by subtracting the amount of residual Si from that calculated from the weight gain, and is shown in Table I. The volatilization of Si in the present work may be attributed to the formation of SiO gas, because the vapour pressure on Si_3N_4 calculated from the weight loss was of the order of 10^{-4} atm and agreed qualitatively with the measured values of Lin [7].

TABLE I The results of the nitridation of Si

Addition	$P^*_{O_2}$	Weight gain (%)	Nitrided Si (%)			α/β	Residual Si (%)	Evap. Si (%)
			α	β	Total			
1 % Fe	P_1	45.4	51	20	71	2.6	22	3
	P_2	46.5	48	37	85	1.3	5	10
	P_3	38.9	35	46	81	0.76	4	14
	P_4	36.5	34	45	79	0.76	5	16
	P_5	43.2	30	53	83	0.57	5	11
1 % Al	P_1	43.4	10	51	61	0.18	23	10
	P_2	36.9	7	68	75	0.10	12	13
	P_3	33.0	6	72	78	0.09	3	19
	P_4	38.5	6	73	79	0.08	7	14
	P_5	44.5	12	70	82	0.16	8	10

$^*P_1 = 1.2 \times 10^{-12}, P_2 = 3.1 \times 10^{-13}, P_3 = 5.8 \times 10^{-14}, P_4 = 8.6 \times 10^{-15}$ and $P_5 = 1.2 \times 10^{-15}$ atm.

TABLE II Free energies of reactions and the equilibrium partial pressures of O_2 and SiO at 1420° C

Equation	ΔG(kcal mol^{-1})*	P_{O_2}† or P_{SiO}‡(atm)
(1) $Fe(s) + \frac{1}{2} O_2(g) = FeO(s)$	−37.285	†2.3×10^{-10}
(2) $Fe(s) + SiO(g) = FeO(s) + Si(1)$	20.772	‡4.8×10^{2}
(3) $Al(l) + \frac{1}{2} N_2(g) = AlN(s)$	−31.206	
(4) $4\ AlN(s) + 3\ SiO_2(s)$ $= Si_3N_4(s) + 2\ Al_2O_3(s)$	−19.745	

*Data for Equation 1 is taken from [10]; all others are from [11].

3.1. The effect of Fe

From the thermodynamic calculation of the equilibrium O_2 pressure (Equation 1, Table II), Fe metal was stable under the conditions studied here. The nitride of Fe is expected to be unstable at high temperatures because it was not found in the reaction product of Si + 10% Fe nitrided at 1350° C for 1 h. Part of the compact was observed to melt, which indicates that Fe was dissolved in the Si to form a low melting point alloy $SiFe_x$.

Acceleration of the nitridation by Fe has previously been concluded to be due to the formation of $SiFe_x$ alloy [6]. Lin [7] observed a decrease in the amount of SiO vapour to below the detection limit of a mass spectrometer when 3.5% Fe powder was added to Si. The effect of Fe addition was suspected as being due to its oxidation to FeO (See Equation 2, Table II). But the reduction of FeO is more probable from the calculation. The presence of $SiFe_x$ promotes the nitridation of Si at 1350° C as already mentioned and results in the high α content. The fact that the α phase was formed at high O_2 pressure and at an early stage of nitridation [12, 13] where the surface layer of SiO_2 played an important role, suggests that the α phase was stabilized by the dissolution of oxygen.

3.2. The effect of Al

The addition of Al promoted the formation of the β phase and retard that of the α phase. The decrease in β at high O_2 pressures is attributed to the retardation of the nitridation reaction. Suzuki [8] and Atkinson *et al.* [14] reported that the formation of the β phase was accelerated when AlF_3 and Al was added respectively.

At an early stage of nitridation, the reaction of Al with N_2 (Equation 3, Table II) together with Si nitridation is expected. Formation of AlN was ascertained by X-ray analysis of an Si + 10% Al compact nitrided at 1350° C for 1 h. The reaction of AlN with surface layer of SiO_2 to form Al_2O_3 and Si_3N_4 (Equation 4, Table II) is, therefore, probably responsible for lowering the effective oxygen potential at the surface of Si particles and retards the formation of the α phase. Formation of Al_2O_3 suggests that its dissolution in Si_3N_4 to form $(Si, Al)_3(N, O)_4$ (sialon) with the β structure [15, 16] may occur, which also lowers the α content in the compact. The reaction of the residual AlN and Al_2O_3 with Si_3N_4 also forms sialon [17].

4. Conclusions

The effect of addition of Fe and Al on the nitridation reaction of Si is investigated under controlled O_2 pressures in the range 1.2×10^{-12} to 1.2×10^{-15} atm. At the highest O_2 pressure, the nitridation reaction is retarded because a protective SiO_2 layer is formed on the Si particles.

Acceleration of the nitridation reaction by addition of Fe is attributed to the formation of the low melting point $SiFe_x$ alloy and that of the α phase at low temperature (1350° C). The predominant formation of the β phase in Al-added Si is based on the formation of Al_2O_3 by Equation 4 (Table II) to lower the oxygen potential. The reaction of Al_2O_3 with Si_3N_4 forms $(Si, Al)_3(N, O)_4$ (sialon); consequently, the β structure is stabilized.

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