Supplementary Information

Oxide additive-free α → β Si_3N_4 phase transformation at 1900 °C

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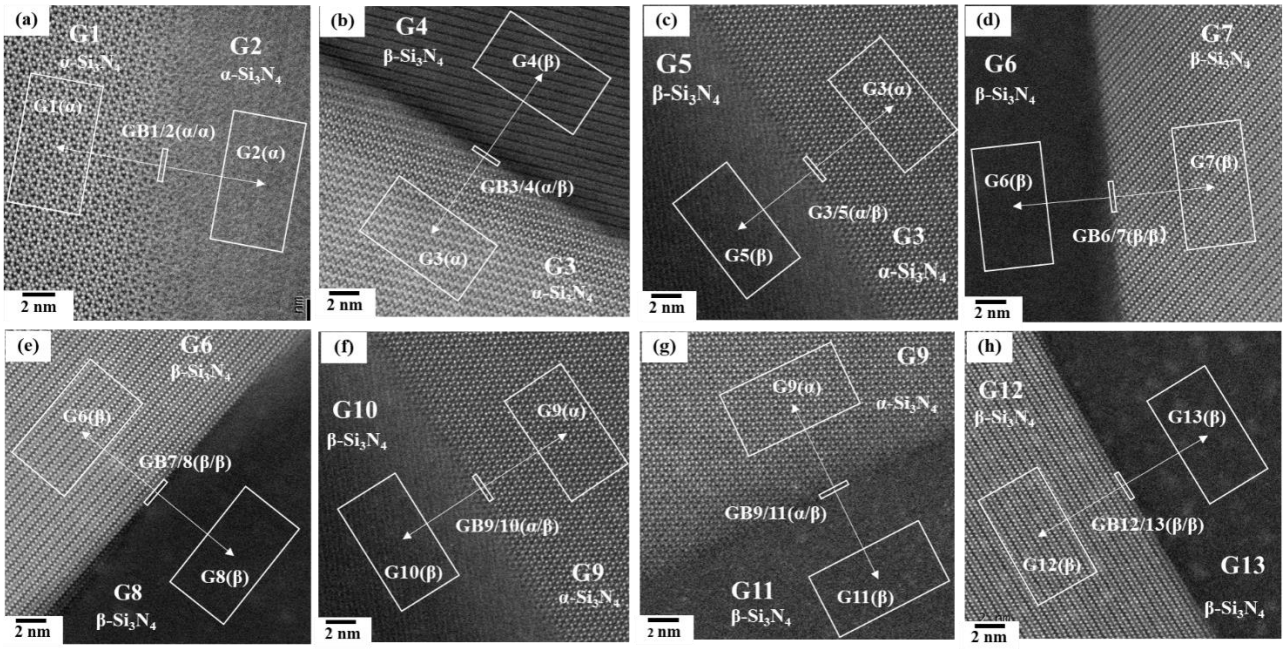

Fig. S1. Position of areas within the Si_3N_4 crystal grains and at the two-grain boundary selected for measuring the oxygen content by TEM-EDS analysis. (a) **G1** and **G2**, (b) **G3** and **G4**, (c) **G3** and **G5**, (d) **G6** and **G7**, (e) **G6** and **G8**, (f) **G9** and **G10,** (g) **G9** and **G11**, and (d) **G12** and **G13**.

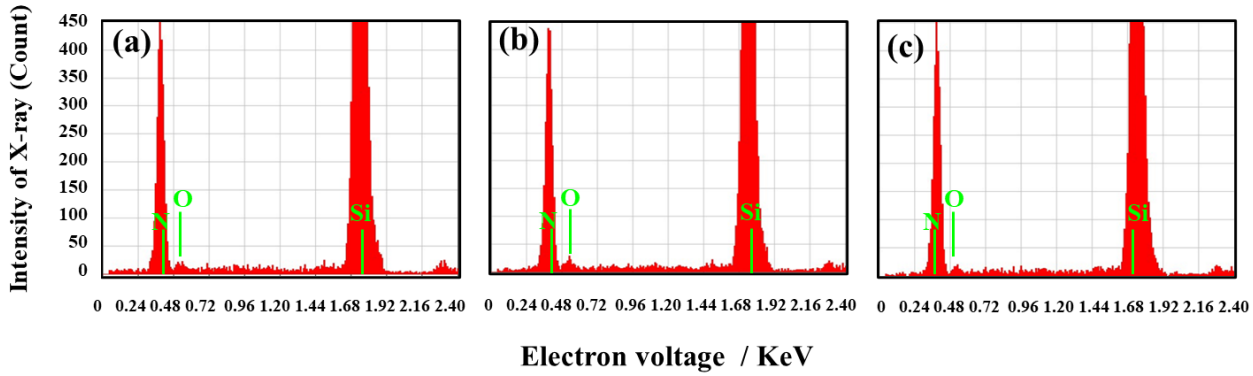

Fig. S2. The spectra obtained by the STEM-EDS area analysis for (a) grain **G1**, (b) grain **G2**, and (c) the two-grain boundary between **G1** and **G2** (**GB1/2**).

Table S1. Impurity oxygen and carbon contents and β-phase content evaluated for Si_3N_4 powder samples.

Heat treatment condition	O [a] (wt%)	C [a] (wt%)	SiO_2 [b] (mol%)	C [b] (mol%)	β-phase content (%)
As-received	1.23	0.11	5.17	1.23	3.7
1600 °C×5 h	1.22	0.13	5.12	1.45	3.2
1800 °C×5 h	0.87	0.09	3.70	1.02	5.7
1900 °C×5 h	0.64	0.07	2.74	0.80	22.6
1900 °C×12 h	0.33	0.05	1.43	0.58	53.5
1900 °C×14 h	0.27	0.04	1.15	0.40	70.2
1900 °C×16 h	0.22	0.05	0.95	0.58	71.8
1900 °C×18 h	0.10	0.04	0.44	0.46	96.5
1900 °C×20 h	0.12	0.01	0.52	0.16	100

a) Elemental analyses for carbon (C) (non-dispersive infrared method, Model C2300, LECO Co., St Joseph, MI, USA) and oxygen (O) (inert gas fusion method, Model ON768, LECO Japan Co., Tokyo, Japan) were performed for the powder samples [12].

b) The chemical composition of the powder samples was evaluated by assuming that 1) all oxygen impurity exists as SiO_2 and 2) the sample powders are composed of Si_3N_4, SiO_2, and free carbon. For evaluating the contents of the SiO_2 and free C, the unit of wt% was converted into mol% by using the mass per unit mole of each component (Si_3N_4:140.286, SiO_2: 60.0848, C:12.016) [12].

Table S2. Silicon, nitrogen and oxygen contents in Si_3N_4 crystal grains and their two-grain boundaries evaluated by STEM-EDS analysis.

Analysis area	Element content (wt%)		
	Si	N	O
G1(α)	79.5	19.5	1.0
GB1/2(α/α)	79.8	19.0	1.2
G2(α)	79.3	19.7	1.0
G3(α)	77.5	21.6	0.9
GB3/4(α/β)	74.4	23.8	1.8
G4(β)	75.1	24.0	0.9
G3(α)	75.1	23.9	1.0
GB3/5(α/β)	76.9	21.9	1.3
G5(β)	78.5	20.8	0.7
G6(β)	75.7	23.9	0.4
GB6/7(β/β)	76.1	22.6	1.3
G7(β)	76.4	23.0	0.6
G6(β)	77.8	21.8	0.4
GB6/8(β/β)	77.4	21.7	0.9
G8(β)	75.1	24.2	0.7

Analysis area	Element content (wt%)		
	Si	N	O
G9(α)	77.2	21.3	1.5
GB9/10(α/β)	76.2	22.2	1.6
G10(β)	75.1	23.5	1.4
G9(α)	76.0	22.7	1.3
GB9/11(α/β)	74.7	23.7	1.6
G11(β)	75.5	23.4	1.1
G12(β)	77.2	22.3	0.5
GB12/13(β/β)	75.4	23.1	1.5
G13(β)	76.3	23.1	0.6