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Enhancement of direct nitridation of silicon by common metals in silicon nitride processing

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Abstract

Catalytic effects of metals, which are often involved in the fabrication of silicon nitride product, on the direct nitridation of silicon were investigated. Silicon granules impregnated with 0.125–2.0% by mass of ytterbium, yttrium, calcium, lutetium, magnesium or cerium were nitrided in a tubular flow reactor operated at temperature in the range of 1300–1390 °C. Enhanced selectivity of α-silicon nitride formation was observed when calcium, yttrium or ytterbium was used. It was also found that a stepwise increase in the nitridation temperature from 1300 to 1390 °C enhanced the conversion of silicon while keeping high content of α-silicon nitride. Yield of α-silicon nitride over 95% was achievable within 3 h of the reaction from an addition of calcium or ytterbium to silicon raw material. It is suggested that characteristic of the impregnated metal, rather than the presence of liquid phase formed during the reaction, has the dominant effects on the α-silicon nitride formation.

Keywords: A. Powders: chemical preparation; D. Si_3N_4; Direct nitridation; Catalyst

1. Introduction

Silicon nitride (Si_3N_4) is one of the most promising structural materials for high-temperature and high mechanical-stress applications because of its excellent properties such as high strength retention at elevated temperature, good thermal shock resistance, high-temperature deformation resistance as well as high corrosion resistance. Two well-known crystal structures of silicon nitride are designated as α-phase and β-phase, respectively. Silicon nitride ceramics are commonly fabricated from α-silicon nitride powder because densification and sintering of α-silicon nitride powder is much easier than sintering of β-powder [1]. Moreover, the fracture toughness of the sintered silicon nitride parts is increased when powder with high content of α-phase is used [2]. The fabrication of silicon nitride parts typically starts from silicon nitride powder, predominantly α-phase, mixed with sintering additives, shaped into a desired component and finally sintered at high temperatures (1700–1800 °C). High content of α-silicon nitride in the starting powder is the very important for making good silicon nitride components.

The direct nitridation of silicon is one of the most commonly used processes to produce silicon nitride powder. It is an inexpensive option for silicon nitride production, but the product usually contains about 92% of α-silicon nitride [3], which is considered as moderately low quality powder. It is therefore desired to increase the content of α-silicon nitride in the product from the direct nitridation of silicon.

It has been known that transition metals can regulate kinetics of silicon nitridation as well as the phase formation [4–8]. However, the metals investigated in the past have been employed in the attempt to understand mechanism of the nitridation. Therefore, metals used are not common elements for silicon nitride processing operation and the impact of the metal residual on the physical properties of the silicon nitride articles has not been reported. Since sintering additives are always used in the fabrication of articles from silicon nitride powder, yet the catalytic effects of the metal species contained in the additive on the nitridation of silicon have not been systematically investigated, it is the objective of this work to investigate the enhancement of the direct nitridation of silicon from elements that have been reported for use as sintering additives, i.e. calcium, yttrium, magnesium, cerium, ytterbium and lutetium [9–11]. It should be noted that, although the effects of calcium and yttrium have already been discussed in

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the previous work from one of the current authors [8], they are included in this study for comparison purpose. In addition, alumina, which is the most common sintering additive for silicon nitride, is not considered in this study because alumina has been reported to enhance the growth of β-silicon nitride [12].

2. Experimental

2.1. Raw material preparation

Raw material used in this study was 300 μm average-sized porous silicon granules composed of 2 μm average-sized grains. The impurities contained in the silicon granules are listed in Table 1. All other physical properties of the granules should be referred to elsewhere [13].

Impregnation of metals onto the silicon raw materials was done by immersing about 10 g of silicon granules in 30 ml of methanol solution of metal-nitrate compounds under continuous agitation using ultrasonic bath. The amount of each metal-nitrate compound dissolved in methanol was adjusted so that a desired level of metal impregnation, e.g. 0.125, 0.45, 1.00 and 2.00% by mass, was achieved after the decomposition and reduction of the nitrate compound at high temperature before the silicon-nitridation reaction. After methanol was completely evaporated, the samples were put in an oven at 110 °C for 24 h to ensure the elimination of moisture as well as possibly remaining methanol.

2.2. Silicon nitride synthesis

For the nitridation of silicon, about 0.5 g of impregnated silicon granules were put into an alumina tray (25 mm × 15 mm × 5 mm deep) and placed in the horizontal tubular flow reactor. The granules were then heated in continuous flow of argon to the predetermined temperature at the rate of 10 °C/min. It has been known that the overall conversion of the direct nitridation at temperature lower than 1300 °C is unacceptably low and the temperature near 1400 °C would result in melting of the silicon raw materials [13]. Moreover, the extent of the nitridation at temperature in the range of 1300 to 1370 °C are roughly constant [8]. Therefore, in this study, the nitridation was conducted only at 1300 and 1390 °C. After the system had reached the prescribed temperature, the granules were pretreated for 1 h with a mixture of 90% argon and 10% hydrogen to remove any native oxide layer on the silicon as well as to convert metal nitrates into reduced metals. Then, the nitridation was initiated by substituting argon feed by nitrogen. The reactant gas mixture was supplied to the reactor at the constant rate of 4.28 l/min. Hydrogen was always supplied into the reactor at the concentration of 10% to prevent the formation of the protective layer, which retarded the progress of the reaction [14]. The nitridation was done for 3 h, since it was shown that the nitridation of silicon granules reached a stage of very slow progress in about 3 h [13].

Table 1
Specification of silicon raw material

Trace impurities (% by mass)				
Fe	Al	Ca	C	O
0.08	0.10	0.02	0.02	0.51

2.3. Characterization

The nitridation product was characterized by powder X-ray diffraction (XRD) using a SIEMENS D5000 diffractometer with Cu Kα radiation. The mass fractions of silicon as well as α- and β-silicon nitride in the product were calculated from the integrated intensity of various peaks of silicon, α- and β-silicon nitride [15]. Surface morphology of the products was observed on JEOL Scanning Electron Microscope (SEM).

3. Results and discussion

3.1. The direct nitridation at constant temperature

The results regarding the effects of different metals on the overall conversion and selectivity of α-phase from 3 h-nitridation at constant temperatures of 1300 and 1390 °C are shown in Figs. 1 and 2, respectively. It is clearly indicated that the addition of metal investigated to silicon raw material results in silicon nitride product containing higher content of α-phase than that obtained from the nitridation of bare silicon. However, most metal investigated affects the extent of reaction

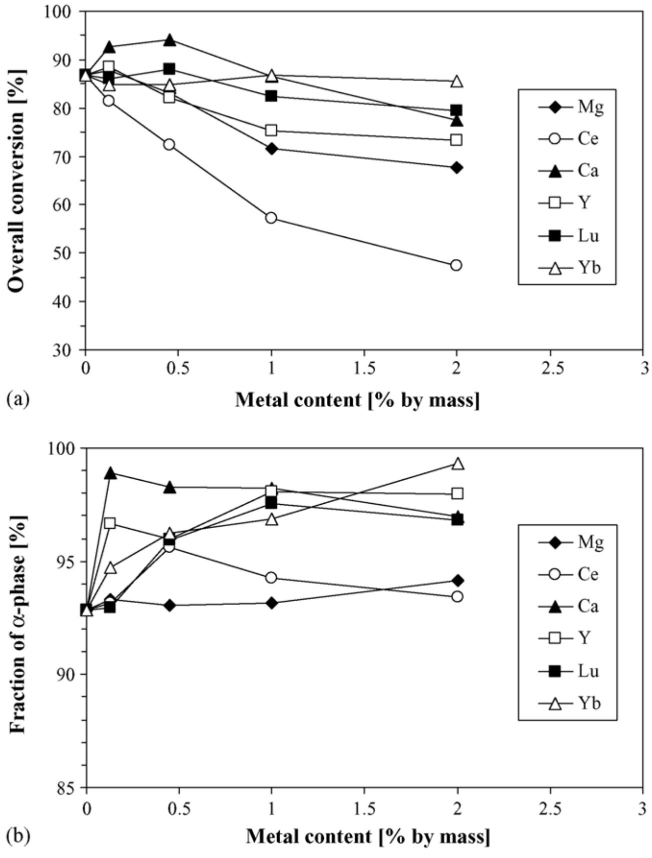

Fig. 1. Effects of different metals on the nitridation of silicon at 1300 °C: (a) overall conversion, (b) fraction of α-phase in silicon nitride product.

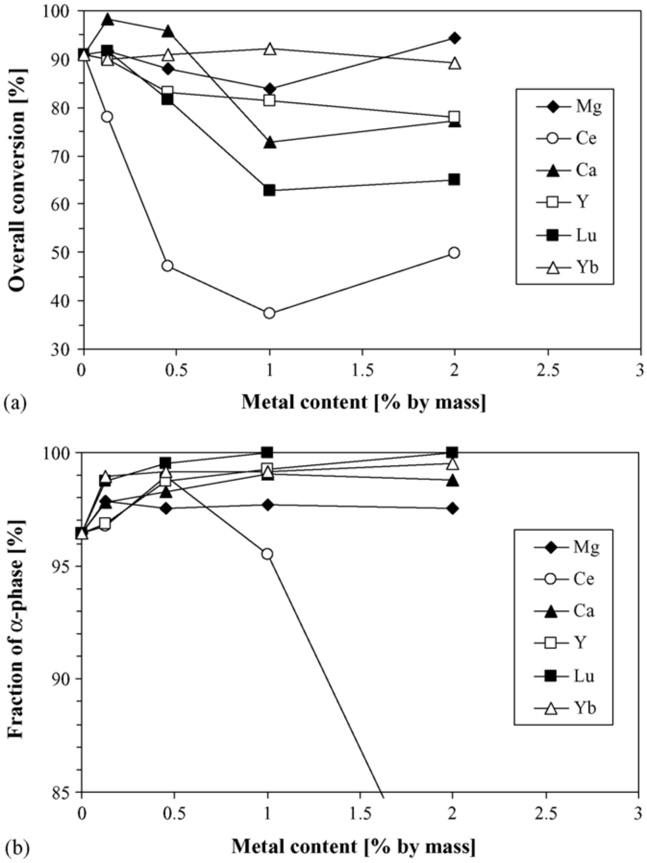

Fig. 2. Effects of different metals on the nitridation of silicon at 1390 °C: (a) overall conversion, (b) fraction of α-phase in silicon nitride product.

as well. The overall conversion is generally decreased when metal is added to the silicon raw material because the metal covering silicon surface hinders direct interaction between nitrogen gas and silicon. It is further found that cerium particularly retards the nitridation of silicon. The reaction is limited to only 50% conversion when 2% by mass of cerium is present in silicon raw materials, regardless of the operating temperature. On the other hand, ytterbium is the only metal investigated that does not affect the overall conversion of silicon nitridation, i.e. ytterbium can improve the fraction of α-silicon nitride without retarding effect on the progress of the reaction. It has been reported that diffusion of silicon atoms to the ytterbium-covered surface is enhanced by thermal treatment at temperature above 700 °C, resulting in the dilution of ytterbium content at the surface [16]. In the other words, ytterbium partially penetrates into silicon substrate at high temperature, allowing nitrogen to directly react with silicon to form silicon nitride.

For the reaction at 1300 °C, calcium, yttrium, lutetium and ytterbium demonstrate greater enhancement in the formation of α-silicon nitride than magnesium and cerium, as shown in Fig. 1b. The content of α-phase in the products obtained from the nitridation of silicon impregnated with one of these four metals is roughly 97%. Over 99% of α-phase is achievable by using silicon impregnated with 2% ytterbium. Calcium is the only metal that can be used in small amount, i.e. as low as 0.125%, to achieve effective suppression of β-phase formation. For yttrium, lutetium and ytterbium, greater amount is required to attain equivalently high fraction of α-phase in the product. However, the use of calcium is not practically preferred since the deterioration in high-temperature strength of sintered silicon nitride parts from calcium impurities has been reported [17]. On the contrary, yttrium, lutetium and ytterbium unlikely cause unfavorable effect on physical properties of sintered products because they have been a part of sintering aid for silicon nitride. Therefore, addition of these metals into silicon raw material is a promising option for the quality improvement of the silicon nitride produced by the direct nitridation process. It should be noted that the results for calcium and yttrium impregnated samples in this work are in agreement with the values reported in the previous work [8].

When the nitridation temperature is increased to 1390 °C, the achieved overall conversion from bare silicon is improved from that obtained at 1300 °C. This behavior is also observed in most of the metal-impregnated silicon (Fig. 2). Only cerium and lutetium present adverse effects with an increase in the reaction temperature. The conversion from the reaction at 1390 °C for silicon impregnated with either cerium or lutetium is significantly lower than the conversion achieved at 1300 °C.

Trend for the selectivity toward α-silicon nitride from the nitridation at 1390 °C with respect to the amount of metal impregnated into silicon is similar to that observed at 1300 °C. However, the selectivity from the reaction at 1390 °C is dramatically improved. Addition of all metals investigated, except cerium, results in the product with fraction of α-phase higher than the nitrided product from bare silicon. Majority of the silicon nitride products contains over 99% of α-phase, which is extraordinarily high for silicon nitride synthesized by the direct nitridation method. On the contrary, cerium is found to be β-silicon nitride enhancer at high temperature. The nitridation of 2% cerium impregnated silicon yields only 79.6% of α-phase (20.4% β-phase). This data was excluded from the plot in Fig. 2b for clarity of the plot.

By comparing SEM micrographs of silicon raw material (Fig. 3a) to that of the silicon nitride product (Fig. 3b), it is indicated that the nitridation of bare silicon is associated with the reaction in gas phase because the surface of the nitrided product is covered by lots of long fibers with diameter in submicrometer range. These fibers are grown via vaporization-condensation type mechanism where siliceous vapor generated from the surface reacts with nitrogen gas in the vapor phase and redeposit as α-silicon nitride whisker [7]. Nevertheless, since the amount of observed fibers cannot account for total mass of the product, it is clear that the direct nitridation process is associated with more than one reaction pathway. Another mechanism proposed in literatures involves gas-solid reaction of nitrogen at the surface of silicon [18]. The formation of silicon nitride via this pathway has been reported to be enhanced by dissociative-chemisorbed nitrogen [7,19].

When metals are impregnated to silicon, morphologies of the resulting nitrided products are different from one sample to another, depending on type of metal impregnated. For lutetium and magnesium impregnated samples (Fig. 3c and d,

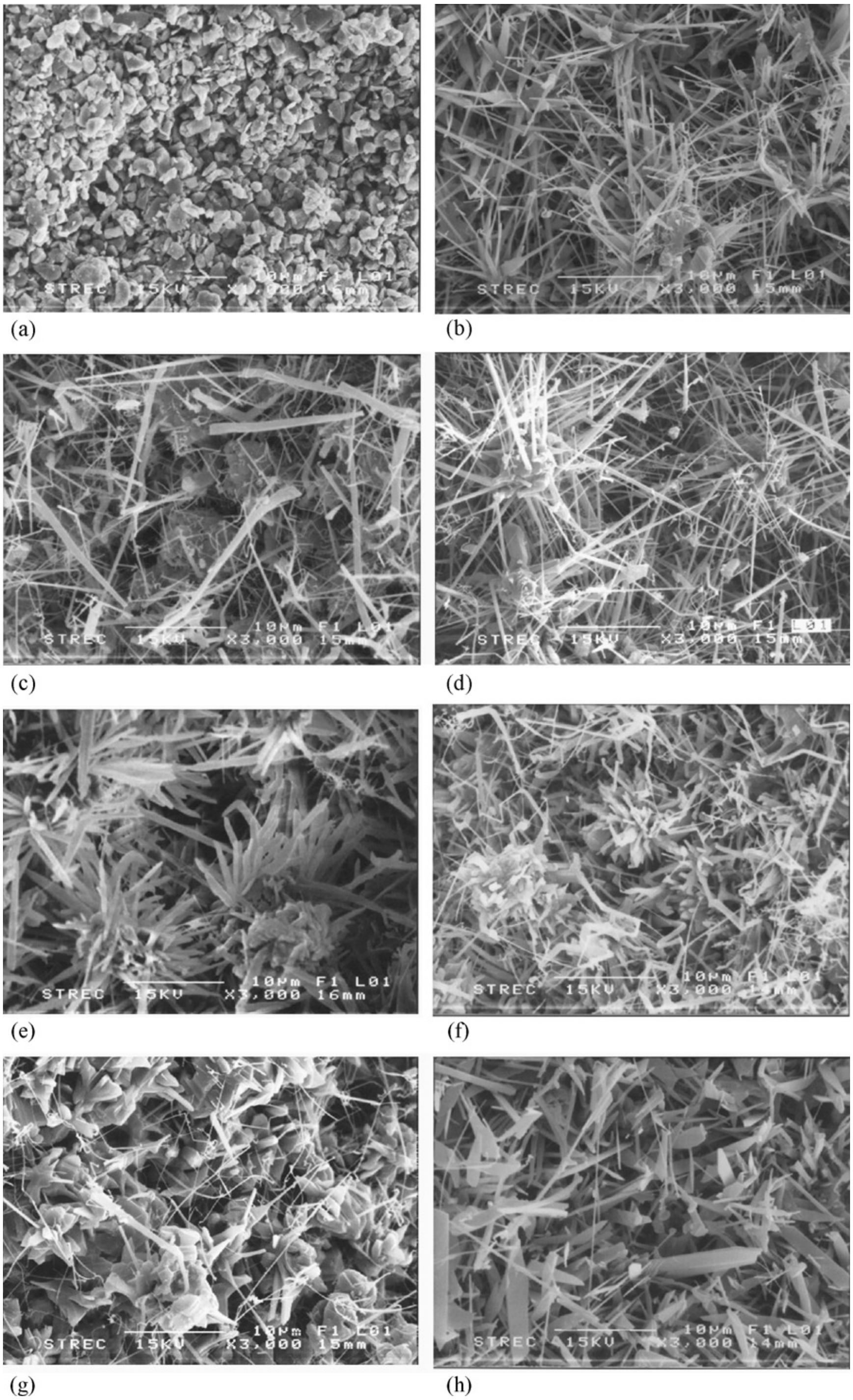
(a) (b) (c) (d) (e) (f) (g) (h)

Fig. 3. SEM images of (a) silicon raw material and products from the nitridation at 1390 °C of: (b) bare silicon, (c) Lu-impregnated silicon, (d) Mg-impregnated silicon, (e) Ca-impregnated silicon, (f) Yb-impregnated silicon, (g) Ce-impregnated silicon, (h) Y-impregnated silicon.

respectively), morphologies of the products are generally close to the product from bare silicon, except the fact that less fibers are observed. On the contrary, samples impregnated with calcium (Fig. 3e) do not have sub-micrometered fibers on the surface. Instead, large non-uniform grains forming bush-like pattern, which seem to grow from particular spot on the surface, are observed. The grains resemble silicon nitride grains grown from liquid silicon, as reported by Shue [20]. Similar observations are also found on ytterbium- and cerium-impregnated samples (Fig. 3f and g, respectively), but size and shape of the grains are different than those observed in calcium-impregnated samples. For yttrium-impregnated samples (Fig. 3h), well-defined rod-like grains are formed without the sign of grain sintering. Therefore, it is suggested that silicon nitride grain grows individually during the reaction when yttrium is present in the system. It should be noted that, according to the energy dispersive X-ray (EDX) analysis, all grains are silicon nitride, regardless of their different morphologies.

3.2. Catalytic effects of metals

The results clearly indicate that the nitridation mechanisms are altered by the presence of metal. Many researchers have claimed that liquid phase resulting from molten alloys of silicon and metal impregnated is a major contributor to the change in reaction mechanism, which, in turn, results in the enhancement of α- and/or β-phase formation [4,7,21]. Since most of the previous studies focused on limited choice of metals and narrow range of metal content, it was inconclusive whether such enhancement was the result from liquid phase or the catalytic characteristic of metal.

The formation of liquid phase from the molten alloy on silicon surface depends upon the operating temperature and concentration of metal in the alloy. However, since actual distribution of metal on silicon surface, i.e. surface concentration of metal, is not known, the presence of liquid on the surface can not be confirmed. Nevertheless, according to data from silicon-metal phase diagram (Table 2), it can be seen that liquid phase is likely present in the system of calcium-, magnesium- and ytterbium-silicon because the reaction temperature in this study (1300 or 1390 °C) is higher than the range of temperature in phase diagram where liquid phase is present. Yet, the nitridation at 1300 °C of silicon impregnated with magnesium shows less significant enhancement in both overall conversion and fraction of α-silicon nitride in the product, comparing to the results from calcium- or ytterbium-impregnated silicon. The results imply that the presence of liquid is not the dominant contributor to the enhancement of α-silicon nitride formation, even though liquid formed may facilitate diffusion of silicon and/or nitrogen during the reaction.

By comparing the results in this work to those reported in literatures, it is interestingly noticed that the formation of α-silicon nitride is enhanced by an addition of metal which is a strong charge donor, e.g. calcium, lutetium, magnesium, ytterbium and yttrium, while no α-phase enhancement, or even enhancement in β-phase, is observed from a weak charge donor or a charge receptor, such as iron, copper, silver, chromium, aluminum and palladium. It should be noted that the electropositivity of metal is categorized by using the standard potential, E° (shown in Table 3) as proposed by Grochala and Edwards [22]. This finding suggests that electronic characteristic of the metal employed contributes to the catalytic effect of metals on the direct nitridation of silicon. Although the actual role of metal on the enhancement of α-silicon nitride formation is still unclear, it has been reported that bond strength of the nitrogen molecule (N_2) during the dissociative adsorption as well as the dissociative adsorption mechanism of N_2 are affected by the presence of a potent charge donor on the surface [23]. Conjoining with the findings that the gas-solid reaction pathway of the silicon nitridation is controlled by N_2 dissociation [7,19,24], it is suggested that the presence of strong charge-donor metal regulates the reaction pathway of the direct nitridation process. Nevertheless, further study is needed to verify the detailed mechanism.

Table 2
Melting points and range of temperature where liquid phase is present in metal-silicon binary systems [25]

Metal	Melting point of metal (°C)	Range of temperature where liquid is present[a] (°C)
Silicon	1414	–
Calcium	842	792–1268
Cerium	798	650–1620
Lutetium	1663	1220–1420
Magnesium	650	637.6–1085
Ytterbium	819	670–1260
Yttrium	1522	1215–1710

[a] Formation of liquid also depends on the concentration of metal in the alloy. In the temperature range reported, liquid is present at certain concentration of metal in alloy.

Table 3
Standard potential, E°, for the respective redox pairs

Redox pair	E° (V)	Redox pair	E° (V)
$Ca^{II}_{(aq)}/Ca^{0}_{(s)}$	−2.87	$Ag^{I}_{(aq)}/Ag^{0}_{(s)}$	+0.80
$Ce^{III}_{(aq)}/Ce^{0}_{(s)}$	−2.34	$Cr^{III}_{(aq)}/Cr^{0}_{(s)}$	−0.74
$Ce^{IV}_{(aq)}/Ce^{III}_{(s)}$	+1.76	$Cu^{II}_{(aq)}/Cu^{0}_{(s)}$	+0.34
$Lu^{III}_{(aq)}/Lu^{0}_{(s)}$	−2.30	$Fe^{III}_{(aq)}/Fe^{0}_{(s)}$	−0.04
$Mg^{II}_{(aq)}/Mg^{0}_{(s)}$	−2.36	$Fe^{II}_{(aq)}/Fe^{0}_{(s)}$	−0.44
$Yb^{III}_{(aq)}/Yb^{0}_{(s)}$	−2.22	$Pd^{II}_{(aq)}/Pd^{0}_{(s)}$	+0.92
$Yb^{II}_{(aq)}/Yb^{0}_{(s)}$	−2.80	$Al^{III}_{(aq)}/Al^{0}_{(s)}$	−1.68
$Y^{III}_{(aq)}/Y^{0}_{(s)}$	−2.37		

3.3. The direct nitridation using stepwise increase in temperature

The results in above section confirm the enhancement of the α-silicon nitride formation by the addition of some common metals to silicon raw materials, especially from the reaction at 1390 °C. However, practical use of these metals is limited by the fact that the achievable overall conversion is not high enough, although the results are promising in term of the content of α-phase in silicon nitride product. Furthermore, agglomeration of the obtained product may occur if the temperature is not well controlled because the nitridation is highly exothermic and 1390 °C is very close to melting point of silicon raw materials. This problem can be overcome by using a stepwise increase in the reaction temperature from 1300 to 1390 °C, as suggested elsewhere [8]. In this work, the reaction was carried out at 1300 °C for 1 h. Then, the temperature was raised at the rate of 10 °C/min to 1390 °C where the system was held at this temperature for 2 h. The reaction gas mixture was maintained during the increase in temperature. After silicon nitride product is formed as the covering shell on silicon raw material by the reaction at 1300 °C, agglomeration due to sintering of silicon can be prevented, even when the temperature is subsequently raised to 1390 °C. The results of the operation with programmed temperature are shown in Fig. 4.

According to Fig. 4, it is clearly illustrated that the overall conversion is significantly improved when the programmed temperature operation is employed. The fraction of α-phase in silicon nitride product remains at relatively high level, although it is not as high as the results from the reaction at 1390 °C. The nitridation of 1% ytterbium impregnated silicon results in

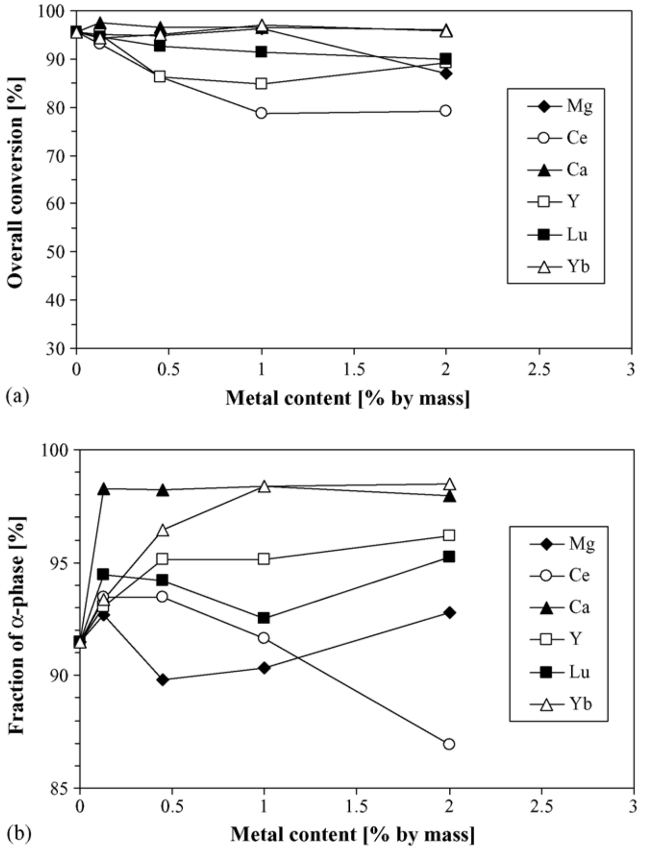

Fig. 4. Effects of different metals on the nitridation of silicon by using the programmed temperature operation: (a) overall conversion, (b) fraction of α-phase in silicon nitride product.

overall conversion of 97% and the product obtained contains over 98% of α-silicon nitride. This result is comparable to the enhancement obtained by using small amount of calcium. However, ytterbium may be more preferable than calcium, because of the deterioration resulted from calcium as mentioned earlier. Nonetheless, further study is needed to investigate effects of residue of these metals on physical properties of sintered products.

4. Conclusion

This work has shown that the enhancement of the direct nitridation of silicon can be achieved by an addition of calcium, yttrium or ytterbium into the silicon raw materials. The direct nitridation of silicon impregnated with calcium as small as 0.125% or ytterbium 2% at 1300 °C results in the product with α-phase content higher than 98%. High fraction of the α-phase can also be obtained from the nitridation at 1390 °C of silicon impregnated with all metals investigated, except cerium. The overall conversion can be dramatically improved, while retaining relatively high fraction of α-phase in the product, by raising the reaction temperature in step-wised fashion, from 1300 to 1390 °C. The effects of the impregnated metal on the nitridation are discussed. It is suggested that characteristic of the impregnated metal, especially electronic characteristic, rather than the presence of liquid phase formed during the reaction, has the dominant effects on the α-silicon nitride formation.

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