Synthesis of SiC layer on metal silicon from SiO by a chemical vapor deposition process

Norihiro MURAKAWA[†], Tomonori IIZUKA, Masanori EGUCHI* and Kohei TATSUMI

Waseda University, Faculty of Science and Engineering, 2-7 Hibikino, Wakamatsu-ku, Kitakyushu 808-0135, Japan

*Fuzzy Logic Systems Institute, 1-5 Hibikino, Wakamatsu, Kitakyushu, Japan

A new process for forming an SiC layer is proposed in which a surface of metal silicon is exposed to gaseous SiO and a gaseous carbon compound at around 1400°C, thereby an SiC layer is formed substantially only on the surface of metal silicon. The resulting SiC layer is of crystalline cubic SiC and a few tens μm in thickness. We consider that the carbon of the SiC layer derives from the gaseous carbon compound and the gaseous SiO promotes the formation of the SiC layer, therefore this process for forming the SiC layer can be defined as one of chemical vapor deposition processes.

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1. Introduction

SiC (silicon carbide) has excellent properties such as oxidation resistance, abrasion resistance and high-temperature strength and SiC coating is thus expected to improve the properties of various materials such as carbon material, heat-resistant metal and ceramic materials.¹⁾ Heretofore, chemical vapor deposition (CVD) processes known to form SiC coating have involved reacting a silane compound and a hydrocarbon with an excessive amount of hydrogen gas at around 1600°C under an argon atmosphere.^{2)–7)}

This study introduces a new CVD process in which granular SiO (silicon monoxide) and toluene as a carbon compound are used to synthesize SiC on metal silicon at around 1400°C. Specifically, the new CVD process can form a crystalline cubic SiC layer of a few tens μm in thickness on the surface of metal silicon and will therefore allow applications as follows: free silicon on SiC sintered bodies resulting from reaction sintering processes can be converted to SiC; an SiC coating can be selectively applied to an intended site by way of coating metal silicon in advance at the site, where SiC is to be coated, and the new CVD process is then applied to the site; and so on.

The new CVD process may be free from the problems in the previous halide CVD processes such as a large amount of hydrogen gas is necessary, coating yield is low due to SiC deposition to other than intended positions, and costly scrubbing of halogen-containing waste gas is necessary.

2. Experimental procedures

2.1 Formation of SiC Layer

300 mg of granular SiO available as a reagent was poured into an alumina crucible with an inner volume of 15 ml, and a support plate of alumina measuring 15×15 and 1 mm thick was placed on the granular SiO, and then a plate of polycrystalline metal silicon (polysilicon plate) measuring 10×10 and 0.75 mm thick or a plate of single-crystal silicon measuring 10×10 and 0.5 mm thick was placed on the support plate, as shown in Fig. 1.

Fig. 1. The configuration for forming SiC layer is prepared such that granular SiO is poured into a crucible, on which an alumina plate and a plate of polysilicon or single-crystal silicon are disposed.

The alumina crucible in this configuration was then disposed into a core tube of a tubular electric furnace and the air within the core tube was exchanged with argon. The alumina crucible was then calcined at 1400°C for 3 h while filling the core tube with toluene vapor. The toluene vapor was supplied from two graphite crucibles that were respectively filled with 15 ml liquid toluene and disposed within the core tube before the calcination, in which one graphite crucible was disposed adjacent to the alumina crucible and another graphite crucible was disposed near one end of the core tube, and a silicone rubber plug inserted to another end of the core tube was penetrated through by a stainless tube of outer diameter 8 mm for venting and measuring the excess pressure within the core tube. We believe that the core tube was filled with toluene vapor during the entire calcination period since the core tube was always maintained at plus pressure.

For comparison, the calcination was carried out in the same configuration except that the granular SiO was not poured into the alumina crucible.

In addition, the calcination temperature of 1400°C was selected in this study by reason that silicon plates considerably deform at higher than 1450°C and SiC is not formed on silicon plates at lower than 1380°C; toluene was selected as the reactant in this study by reason that SiC layers could be more easily formed than methanol, ethanol, acetone, isopropyl alcohol, ethylene glycol, and xylene in our previous experiments.

[†] Corresponding author: N. Murakawa; E-mail: n-murakawa@kmh.biglobe.ne.jp

2.2 Evaluation

SiC layers formed on the polysilicon or single-crystal silicon plates by means of the above-noted procedures were determined using an X-ray diffraction (XRD) apparatus. The SiC layers were also observed using a scanning electron microscope (SEM) and analyzed by energy dispersive X-ray (EDX) spectroscopy for elemental content and electron back scatter diffraction for crystal orientation.

3. Results

Figure 2 shows perspective SEM-images of fractured polysilicon plates of (a) uncalcined polysilicon plate, (b) polysilicon plate calcined with SiO at 1400°C for 3 h, and (c) polysilicon plate calcined without SiO at 1400°C for 3 h. As seen from Fig. 2, the polysilicon plates maintained their plate shapes respectively even after calcination, but the calcination somewhat affected the surface texture of the polysilicon plates.

Figure 3 shows SEM-images in back scattered electron mode of polished fracture surfaces of (b) polysilicon plate calcined with SiO at 1400°C for 3 h and (c) polysilicon plate calcined without SiO at 1400°C for 3 h, in which each polysilicon plate was embedded in epoxy resin and then polished for each fracture

Fig. 2. Perspective SEM-images of fractured polysilicon plates: (a) uncalcined polysilicon plate, (b) polysilicon plate calcined with SiO at 1400°C for 3 h, and (c) polysilicon plate calcined without SiO at 1400°C for 3 h.

Fig. 3. SEM-images of polished fracture surfaces of (b) polysilicon plate calcined with SiO at 1400°C for 3 h and (c) polysilicon plate calcined without SiO at 1400°C for 3 h.

surface. From elemental analysis using SEM-EDX in Figs. 3(b) and 3(c), the sites indicated as “Silicon” substantially consist of silicon and the sites indicated as “Formed Layer” substantially consist of silicon and carbon. Figures 3(b) and 3(c) also demonstrate that the “Formed Layer” calcined with SiO is thicker and includes less pores in comparison with the “Formed Layer” calcined without SiO.

Elemental contents of silicon and carbon in the “Formed Layer” were measured using SEM-EDX by randomly selecting 10 measuring points in each “Formed Layer” of the polished fracture surfaces. The resulting 10 measured values were averaged and represented as Si/C atomic ratio in **Table 1**. The Si/C atomic ratios in Table 1 indicate that the composition of the “Formed Layer” calcined with SiO substantially corresponds to the SiC composition of Si/C = 1/1 whereas the content of carbon is larger than that of silicon in the “Formed Layer” calcined without SiO.

The calcination also affected the weight of polysilicon plates, i.e. there appeared weight loss of 4% in (b) polysilicon plate calcined with SiO and 11% in (c) polysilicon plate calcined without SiO as shown in Table 1.

Figure 4 shows three XRD patterns of silicon plates of (a) uncalcined polysilicon plate, (b) polysilicon plate calcined with SiO, and (c) polysilicon plate calcined without SiO. In the measurement of XRD, X-rays were irradiated to and diffracted from the upper surfaces of polysilicon plates shown in Fig. 2. There is a significant difference between the XRD patterns of (b) polysilicon plate calcined with SiO and (c) polysilicon plate calcined without SiO, i.e. the XRD pattern of (b) polysilicon plate calcined with SiO displays sharp peaks that completely correspond to the standard peaks of cubic SiC whereas the XRD pattern of (c) polysilicon plate calcined without SiO displays relatively weak peaks of cubic SiC as well as one weak peak of silicon.

Furthermore, **Fig. 5** shows perspective SEM-images of fractured single-crystal silicon plates of (d) uncalcined single-crystal silicon plate, (e) single-crystal silicon plate calcined with SiO at

Table 1. Comparison of Si/C atomic ratio in formed layer and weight loss in polysilicon plate and single-crystal silicon plate between calcined with and without SiO

Calcination	polysilicon plate		single-crystal silicon plate	
	with SiO	without SiO	with SiO	without SiO
Weight loss	4%	11%	2%	6%
Si/C atomic ratio	1.01	0.87	1.02	0.91

Fig. 4. X-ray diffraction patterns of silicon plates: (a) uncalcined polysilicon plate, (b) polysilicon plate calcined with SiO at 1400°C for 3 h, and (c) polysilicon plate calcined without SiO at 1400°C for 3 h.

Fig. 5. Perspective SEM-images of fractured single-crystal silicon plates: (d) uncalcined single-crystal silicon plate, (e) single-crystal silicon plate calcined with SiO at 1400°C for 3 h, and (f) single-crystal silicon plate calcined without SiO at 1400°C for 3 h.

Fig. 6. SEM-images of polished fracture surfaces of (e) single-crystal silicon plate calcined with SiO at 1400°C for 3 h and (f) single-crystal silicon plate calcined without SiO at 1400°C for 3 h.

1400°C for 3 h, and (f) single-crystal silicon plate calcined without SiO at 1400°C for 3 h. In cases of single-crystal silicon plates, the plates also maintained their plate shapes respectively even after calcination, but there appeared a large number of small projections on the entire surfaces of plates as seen from Fig. 5.

Figure 6 shows SEM-images of polished fracture surfaces of (e) single-crystal silicon plate calcined with SiO at 1400°C for 3 h and (f) single-crystal silicon plate calcined without SiO at 1400°C for 3 h, in which each single-crystal silicon plate was embedded in epoxy resin and then polished for each fracture surface. From elemental analysis using SEM-EDX in Figs. 6(e) and 6(f), the sites indicated as “Silicon” substantially consist of silicon and the sites indicated as “Formed Layer” substantially consist of silicon and carbon. Figures 6(e) and 6(f) also demonstrate that the “Formed Layer” calcined with SiO is thicker in comparison with the “Formed Layer” calcined without SiO.

Similarly to the cases of polysilicon plates, elemental contents of silicon and carbon in the “Formed Layer” were measured using SEM-EDX by randomly selecting 10 measuring points in each “Formed Layer” of the polished fracture surfaces. The resulting 10 measured values were averaged and represented as

Fig. 7. X-ray diffraction patterns of silicon plates: (d) uncalcined single-crystal silicon plate, (e) single-crystal silicon plate calcined with SiO at 1400°C for 3 h, and (f) single-crystal silicon plate calcined without SiO at 1400°C for 3 h.

Si/C atomic ratio in Table 1. The Si/C atomic ratios in Table 1 also indicate that the composition of the “Formed Layer” calcined with SiO substantially corresponds to the SiC composition of Si/C = 1/1 whereas the content of carbon is larger than that of silicon in the “Formed Layer” calcined without SiO.

The calcination also affected the weight of single-crystal silicon plates, i.e. there appeared weight loss of 2% in (e) single-crystal silicon plate calcined with SiO and 6% in (f) single-crystal silicon plate calcined without SiO as shown in Table 1.

Figure 7 shows three XRD patterns of silicon plates of (d) uncalcined single-crystal silicon plate, (e) single-crystal silicon plate calcined with SiO at 1400°C for 3 h, and (f) single-crystal silicon plate calcined without SiO at 1400°C for 3 h. In the measurement of XRD, X-rays were irradiated to and diffracted from the upper surfaces of single-crystal silicon plates shown in Fig. 5. The XRD pattern of (d) uncalcined single-crystal silicon plate has only one peak at about 28°, the XRD pattern of (e) single-crystal silicon plate calcined with SiO has the peaks of 3C SiC and weak peaks of silicon, and the XRD pattern of (f) single-crystal silicon plate calcined without SiO has also the peaks of 3C SiC and weak peaks of silicon. Comparing the XRD patterns of (e) and (f), the pattern of (e) has relatively strong peaks of 3C SiC and weak peaks of silicon.

In addition, when polysilicon plates were calcined with SiO at 1400°C in the configuration shown in Fig. 1, SiC was generated substantially only on the surfaces of polysilicon plates, i.e. SiC was not generated on the surfaces of the alumina crucible, the support plate of alumina, etc. All the SiC layers resulting from the calcination with SiO at 1400°C were not removed from silicon plates under Scotch tape peel test.

Figure 8 shows the mapping of crystal orientation of (i) polysilicon plate calcined with SiO at 1400°C for 3 h and (ii) single-crystal silicon plate calcined with SiO at 1400°C for 3 h. The mapping demonstrates that crystal orientation of SiC is random in each of the formed layers no matter whether the initial silicon plate is polysilicon or single-crystal silicon, and the color change in silicon regions suggests that recrystallization occurred in both of polysilicon and single-crystal silicon.

4. Discussion

From the observation of the silicon plates of polysilicon and single-crystal after the calcination at 1400°C, SiC layers have been generated on their surfaces, surface shapes have been deformed to some extent, and their weights have been decreased

Fig. 8. Mapping of crystal orientation in Y direction: (i) polysilicon plate calcined with SiO at 1400°C for 3 h, and (ii) single-crystal silicon plate calcined with SiO at 1400°C for 3 h.

somewhat. These results indicate that vaporizing and semi-melting occur in the silicon plate to a certain degree when SiC layers are formed under the calcination at 1400°C.

In view of the results described above, existence of SiO in the calcination of silicon plates considerably promotes the generation of SiC on the silicon plates such that the resulting SiC layer is thicker and the composition thereof is substantially Si/C = 1/1.

Furthermore, SiC is synthesized substantially only on the surfaces of silicon plates rather than on other wider surfaces.

Based on these results, we consider that some cause occurs on the surfaces of silicon plates, thereby making possible to generate SiC at a temperature lower than the temperatures at which gaseous SiO and toluene vapor react directly to synthesize SiC.

Although no more than a mere idea, the cause may be some interaction between SiO and metal silicon such as exchanging of O atom to generate active Si*, for example, then the resulting active Si* may lead to the generation of SiC at lower temperatures as follows:

5. Summary

In previous papers where SiO appears in relation to SiC synthesis, the SiO is often no more than an idea or concept as an intermediate compound for synthesizing SiC.^{8),9)} In this study, commercially available SiO itself was used, consequently a new CVD process for forming an SiC layer on metal silicon can be proposed in which SiO promotes to form the SiC layer on the metal silicon. This new CVD process may provide specific advantages such as free silicon on SiC sintered bodies can be converted to SiC and an SiC coating can be selectively applied to an intended site on surfaces of complex shapes, in particular.

References

- 1) M. Takegoshi, F. Ono, K. Ogawa and M. Sato, *Ceramics*, **49**, 1026–1029 (2014) [in Japanese].
- 2) M. A. Pickering and J. L. Triba, *Ceramics*, **42**, 426–430 (2007) [in Japanese].
- 3) S. Aoyama and N. Shibata, *J. Ceram. Soc. Japan*, **102**, 13–17 (1994).
- 4) W. R. Haigis and M. A. Pickering, *Mater. Des.*, **14**, 130–132 (1993).
- 5) J. S. Goela, M. A. Pickering and L. E. Burns, *Proc. SPIE*, **2855**, 2–13 (1996).
- 6) J. S. Goela and M. A. Pickering, *Ceram. Eng. Sci. Proc.*, **19**, 579–581 (1999).
- 7) D. Zhu, P. Hing, P. Brown and Y. Sahai, *J. Mater. Process. Technol.*, **48**, 517–523 (1995).
- 8) “SiC Ceramics”, Ed. by S. Somiya and Y. Inomata, Published by Uchida Rokakuho Publishing Co. (1988) [in Japanese].
- 9) H. Tanaka, *J. Ceram. Soc. Japan*, **119**, 218–233 (2011).