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SciVerse ScienceDirect
Journal of the European Ceramic Society 32 (2012) 2565–2571
www.elsevier.com/locate/jeurceramsoc

Preparation and characterization of freestanding SiC(Ti, B) films derived from polycarbosilane with TiN and B as additives

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Received 5 September 2011; received in revised form 20 January 2012; accepted 6 February 2012
Available online 3 March 2012

Abstract

Freestanding SiC(Ti, B) films with high temperature resistance were fabricated from polymer precursor of polycarbosilane (PCS) blended with 0.26 wt% TiN and 0.74 wt% B powders. Results reveal that SiC(Ti, B) films with good mechanical properties are uniform and dense. After high temperature annealing at 1500 °C in argon, SiC(Ti, B) films exhibit better high temperature resistance as compared to SiC films without additives, which implies their potential applications in ultra-high temperatures (exceeding 1500 °C) microelectromechanical systems (MEMS). Sintering additives are effective in suppressing the growth of SiC crystals and decreasing the content of oxygen and free carbon, which is normally beneficial to enhance high temperature resistance of films.

Keywords: Films; Microstructure-final; Mechanical properties; SiC; Microelectromechanical systems

1. Introduction

Microelectromechanical systems (MEMS), which have been developed over approximately the past two decades using Si micromachining technology, have been applied in many fields, such as automotive, aerospace, ship, nuclear power instrumentation, satellites, space exploration, geothermal wells and sensors. Recently, there are increasing demands for MEMS devices that can operate in harsh environments, including high temperatures and severe mechanical and chemical conditions.[1–5] However, the applications of Si-MEMS in harsh environments are limited due to the inherent physicochemical properties of Si.

Among various semiconductor materials, silicon carbide (SiC) is well known as an attracting material for high power, high voltage and high frequency as well as high-temperature microelectronics because of its wide band gap, high thermal conductivity, high electric breakdown field and high saturation velocity. Moreover, outstanding mechanical and chemical properties with respect to Si make SiC a leading candidate for MEMS in a variety of harsh conditions, ranging from highly corrosive to highly erosive environments.[6–8] So far, chemical vapor deposition (CVD), physical vapor deposition (PVD), atomic layer epitaxy, molecular beam epitaxy, sputtering, or laser ablation have been successfully employed to deposit single and polycrystalline forms of SiC thin films on substrate.[9–12] And each technique has its own merits and limitations. However, the formation of voids and defects are observed at the SiC/substrate interface in the initial stage of the growth, which leads to serious problems in the realization of SiC MEMS devices.[13] In addition, the SiC films have a large residual stress caused by the 8% thermal expansion coefficient difference and over 20% lattice mismatch which occurs during high temperature SiC films growth on substrate.[14] Therefore, there has been a considerable amount of interest in the development of alternative technique for producing SiC films to overcome these difficulties.

Previous works on a novel processing technique for making SiC MEMS from polymeric precursors referred to as polymer-derived ceramics (PDC) have been reported. Chung have used a polydimethylsilazane (PDMS) mold to fabricated SiCN microstructures for a high-temperature environment (exceeding 1400 °C).[2] Liew et al. have reported another method of using precursor photopolymerization as a simpler alternative to micro casting as a fabrication technique for SiCN MEMS, which is capable of withstanding over 1500 °C.[15] Jang et al. have

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doi:10.1016/j.jeurceramsoc.2012.02.004

fabricated polymer-derived microstructured SiC ceramic films applying a softlithographic technique. The Young's modulus determined by nanoindentation is 110 GPa after crystallization at 1500 °C.[16] The method would be more actual for the fabrication of MEMS, and the obtained SiC films have highly attractive shaping properties and elevated temperature resistance. However, there are still some disadvantages, such as cantilever structure curling, demolding difficulty and the large difference of shrinkage ratio between the SiC and substrate, which causes serious defects.

Our previous work has introduced a technique based on melt spinning of precursor to produce continuous freestanding SiC films with high modulus and high density which could avoid significant difference of thermal expansion coefficient resulted from heteroepitaxial techniques.[17] Freestanding SiC films possess superior mechanical properties and chemical inertness, which are of great interest in fabricating MEMS for applications in high temperature or harsh environments. However, the films do not remain mechanically stable at temperatures above 1200 °C. Many attempts of doping have been applied to improve their thermal stability. Therefore, the aim of the present study is to prepare continuous freestanding SiC(Ti, B) films with desired properties by melt spinning Ti, B-containing polycarbosilane (TiB-PCS) precursor, since Ti and B have been found to be very effective in promoting the densification of polymer-derived SiC materials, as demonstrated by the fabrication of Sylramic^{TM} SiC fibers.[18] Microstructure, physical properties and heat-resistant performance of SiC(Ti, B) films were characterized to provide a detailed understanding of the multiphase formation. Effects of TiN, B sintering additives on the structural evolution were also investigated.

2. Experimental procedure

2.1. Preparation of SiC(Ti, B) film

PCS samples (Si: 41.03 wt%, C: 43.24 wt%, O: 1.05 wt%) employed in our laboratory were synthesized at high temperature and high pressure by thermal decomposition of polydimethylsilane (PDMS) following the work by Yajima et al.[19–21] They are transparent solid with a number average molecular weight of 1426 and a weight average molecular weight of 3296, which were determined by gel permeation chromatography (GPC). The GPC measurements were performed at 35 °C with THF as the eluant (1.0 ml/min) using an Agilent 1100 system (Agilent, Santa Clara, CA, USA). They have a melting point of 215 °C. TiN (purity >99%, Shanghai Longjin Metallic Material Co., Ltd., China) and B (purity 94–96%, Shanghai Longjin Metallic Material Co., Ltd., China) powders were used as the sources of Ti and B. Their initial particle sizes measured by Laser Particle Sizer (LS-603, OMEC, China) are $d_{50} = 1.47$ and 1.26 μm, respectively. According to the preliminary experiments, the TiN and B concentrations in the precursor were fixed to 0.74% and 0.26% on the basis of the PCS mass, respectively. The particle size was further reduced to $d_{50} < 300$ nm by ball milling. The TiN and B powders were added into the PCS/xylene solution and then homogenized by ball milling and ultrasonic agitation processing. The xylene was removed afterwards completely by vacuum distillation at 110 °C to yield TiB-PCS precursors.

The TiB-PCS precursors charged into the spinning device were first deaerated for 3 h in the vacuum deaeration furnace under 250 °C, and then melt spun into green films using a melt spinning machine (MMCH05, Chemat) under 220 °C at an extrusion rate of 0.3 mm/min. The thickness of green films was controlled by adjusting the spout size of the spinneret mouth and spinning speed. The as-spun green films were treated with oxidation-induced crosslinking in air at a flow rate of 200 ml/min with a heating rate of 3 °C/min and held for 3 h at 180 °C.

The cured TiB-PCS films were presintered in argon at a flow rate of 200 ml/min with a heating rate of 5 °C/min to 900 °C, 950 °C, 1000 °C and held for 30 min, respectively. This pyrolysis converted the translucent cured films into lustrous black ceramic films. Then the films were finally sintered at 1800 °C in high-purity argon at a ramp rate of 40 °C/min and maintained for 10 min. In addition, SiC films without sintering additive employed in this study were produced in our laboratory. SiC(Ti, B) films and SiC films were heat-treated under argon atmosphere at a flow rate of 200 ml/min with a heating rate of 40 °C/min and held for 1 h at 1500 °C.

2.2. Analysis and characterization

Morphology of the films was examined by scanning electron microscope (SEM) (Model 1530, LEO, Germany), and their composition and microstructure were characterized by Fourier transform infrared spectrometer (Nicolet Avatar FTIR 360, USA), Raman spectrometer (LabRam I, Dilor, France), X-ray diffractometer (XRD) (X'pert PRO, Panalytical, Netherlands) and electron probe microanalysis (EPMA) (JXA-8100, JEOL, Japan). Mechanical properties of SiC(Ti, B) films were tested by Microhardness Tester (HV-1000, Nboeo Detecting Instrument, China) and Universal Testing Machine (Sun 2500, Galdabini, Italy) according to ASTM D3379-75 procedure, and film density was measured by floatation method based on Archimedes principle using CH_2I_2 (3.32 g/cm^3) and $CHCl_3$ (1.48 g/cm^3) as the liquid couple.

3. Results and discussion

3.1. Chemical structure analysis

The crosslinking and pyrolysis processes of SiC(Ti, B) films were studied by FTIR. The FTIR spectra in Fig. 1 exhibits that the adsorption peak of Si–H stretching at 2100 cm^{-1} in the cured films are evidently weaker compared with that of PCS green films, which is mainly resulted from the oxidation of terminal Si–H groups in the PCS and formation of Si–O–Si bonds. Furthermore, the intensity of adsorption peak at 1020 cm^{-1}, induced by Si–C–Si stretching of Si–CH_2–Si, enhances owing to the increase of Si–O–Si.[19,22] In addition, a part of Si–CH_3 groups could be oxidized into Si–COOH, which leads to the appearance of adsorption peak at 1710 cm^{-1}.

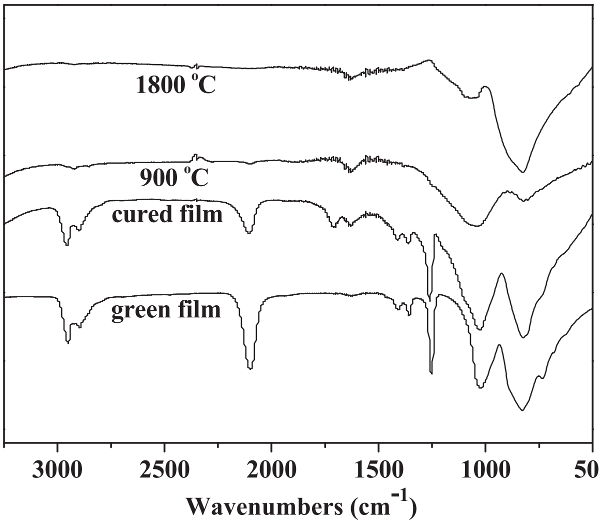

Fig. 1. FTIR spectra for continuous freestanding SiC(Ti, B) films.

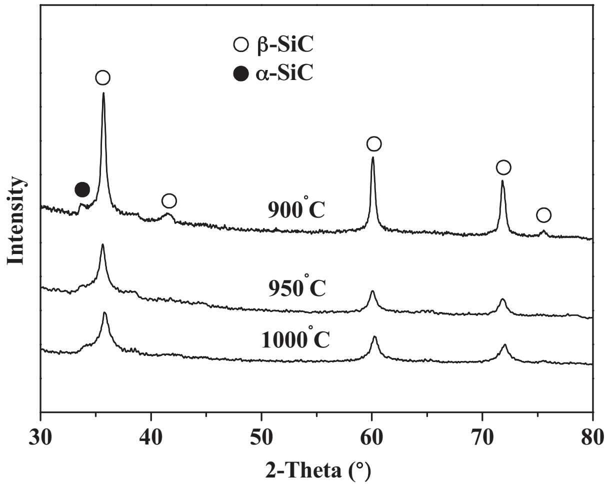

Fig. 2. XRD of SiC(Ti, B) films with different presintering processes.

Since no chemical reaction occurs between sintering additives and PCS, no corresponding peak could be detected by FTIR.

For the films pyrolyzed at 900 °C, the Si–H peak of 2100 cm^{-1} and the Si–CH_3 peak of 1250 cm^{-1} are both shifted to lower wavelength, owing to the pyrolysis reaction at 500–900 °C that organic PCS is converted into SiC ceramic with the debonding of Si–H and Si–CH_3. The adsorption peaks of C–H stretching of Si–CH_3 at 2950 cm^{-1} and 2900 cm^{-1} and Si–C–Si at 700–800 cm^{-1} also become weaker due to the cleaving of the C–H and Si–C bonds in the PCS at about 900 °C.[23–25] As a result of the decomposition of SiO_xC_y phase above 1000 °C,[26,27] the intensity of adsorption peak at 1020 cm^{-1} decreases with the rise of pyrolysis temperature.

3.2. *Effects of presintering temperature on the microstructure of sintered SiC(Ti, B) films*

Structure and morphology of sintered SiC(Ti, B) films with different presintering processes were studied using XRD, Raman and SEM analysis. The XRD patterns in Fig. 2 show three main sharp peaks which are assigned to the diffraction (1 1 1) ($2\theta = 35.528°$), (2 2 0) ($2\theta = 59.862°$) and (3 1 1) ($2\theta = 71.758°$) planes of β-SiC phase, respectively. The intensity of the β-SiC diffraction peaks decreases with the rise of presintering temperature. The average crystallite sizes of β-SiC grains in the films presintered at 900, 950 and 1000 °C were calculated to be 86 nm, 35 nm and 23 nm using Scherrer equation calculated from the half-value width of the (1 1 1) peak, respectively. Since β-SiC seed crystals could be formed at 1000–1300 °C,[28,29] the films presintered at close to the range of temperature could help to improve the density of seed crystals and suppress the grain growth during the pyrolysis process. Namely, the films presintered at 900 °C with relatively low density of seed crystals would have large grain size after sintering at 1800 °C. Grain size is one of the important factors to mechanical properties of polymer-derived SiC material.[30] Generally, films with large grain size possess relatively low strength. In addition, α-SiC identified by one additional peak at 34.088° is present in the films presintered at 900 °C, indicating that some β-SiC transforms into α-SiC, which may be responsible for the heavy stacking faults.[31]

Free carbon content is an important factor for antioxidation property of polymer-derived SiC material.[32] And Raman spectroscopy is one of the most sensitive spectral methods to characterize the different modifications of carbon.[33] Fig. 3 depicts the Raman spectra of sintered SiC(Ti, B) films with different presintering temperatures. The intensity of the peaks at 1347 cm^{-1} (D band) and 1600 cm^{-1} (G band) is proportional to the amount of free carbon clusters in the films.[33,34] The spectra shows that the D band and G band of SiC(Ti, B) films presintered at 900 °C are much sharper than others, suggesting that a large proportion of the carbon atoms segregate into clusters during pyrolysis. Free carbon in the films could be further oxidized into gaseous species at high temperatures, which generate many pores and cause more serious breakage and mechanical property

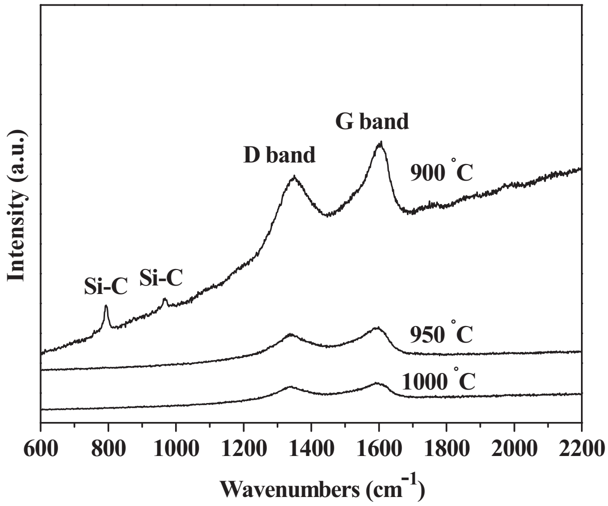

Fig. 3. Raman spectroscopy of freestanding SiC(Ti, B) films with different presintering temperatures.

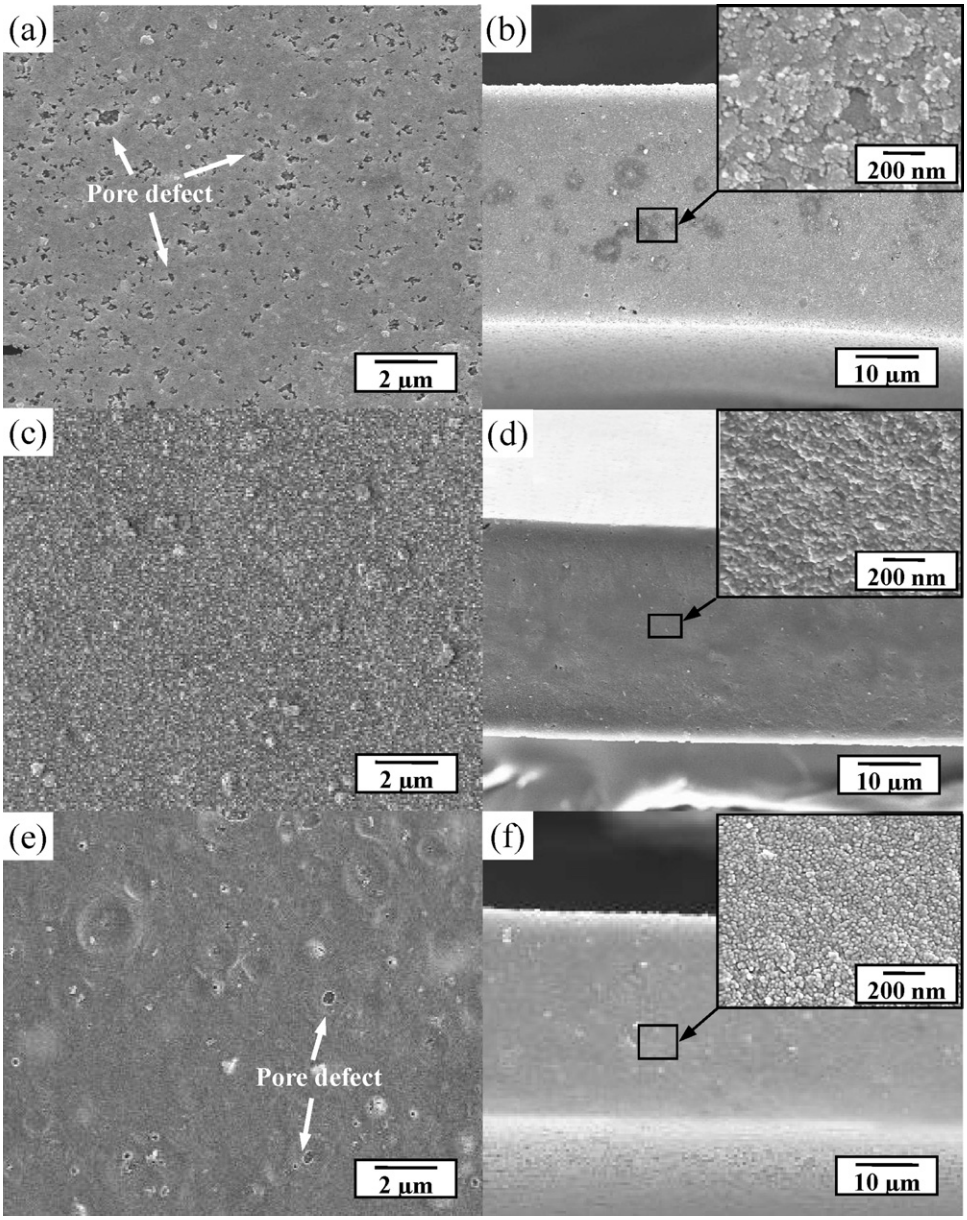

Fig. 4. SEM images of freestanding SiC(Ti, B) films. (a) Surface and (b) cross-section of pyrolyzed sample presintered at 900 °C; (c) surface and (d) cross-section of pyrolyzed sample presintered at 950 °C; (e) surface and (f) cross-section of pyrolyzed sample presintered at 1000 °C.

degradation.[32] In addition, Raman scattering efficiency of carbon species can be assumed to be at least ten times higher than that of pure SiC materials, owing to their optical absorption.[35] Therefore, two weak sharp lines at about 790 and 967 cm^{-1} attributed to β-SiC can be only observed in films presintered at 900 °C, although the SiC nanocrystals are present well in the ones with other presintering processes which are identified by XRD (in Fig. 2). This result also reveals that the samples presintered at 900 °C have lager grain size of β-SiC, which is in a good agreement with XRD analysis.

Fig. 4 shows the surface and cross-section morphologies of sintered SiC(Ti, B) films with different presintering processes. It can be clearly observed that the sintered films presinteried at 950 °C are dense and uniform under high magnification, whereas a lot of pore defects are detected and distributed uniformly on the surface as well as the cross-section of the one presintered at 900 °C. Formation of these pore defects might be related to the volatilization of B_2O_3 in the pyrolysis process, which generated by the oxidation of B in the crosslinking process, and then partly volatilized during the presintering process above 900 °C.[36] However, excess B_2O_3 leaves in the films after being presintered at low temperature and will volatilize in sintering processes, which produces pore defects in the films. Moreover, the excess volatilization of B_2O_3 leads to inadequate content of B in the films presintered at 1000 °C for promoting the densification in sintering process, and results in the defects in films. Therefore, it is revealed that presintering process is the key factor to get uniform and compact SiC(Ti, B) films, the density of seed crystals and content of B in the presintered films are influenced deeply by the presintering temperature as mentioned above.

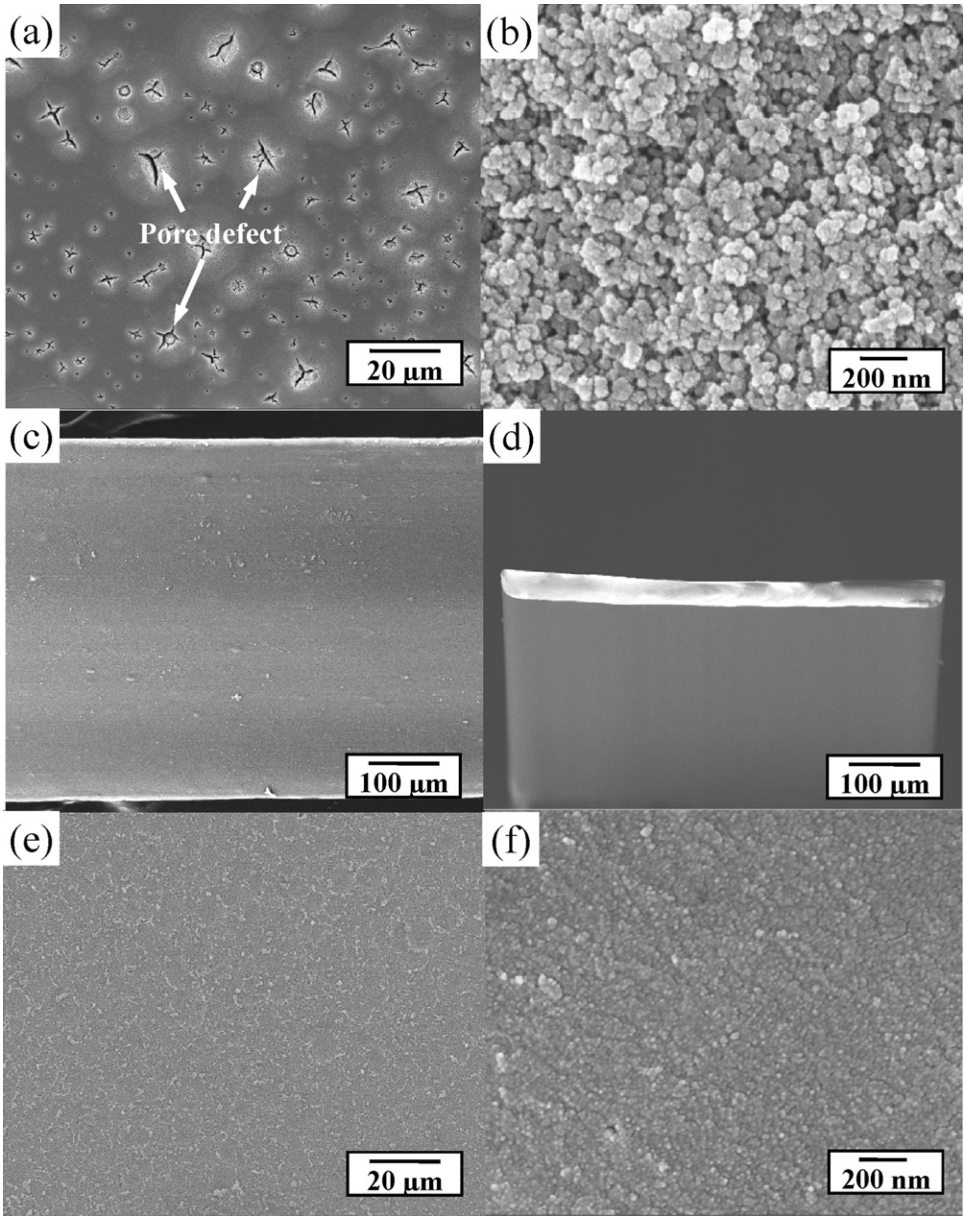

Fig. 5. SEM images of the samples annealed in Ar at 1500 °C for 1 h. (a) Surface and (b) cross-section enlargement of SiC films; (c) surface and (d) cross-section of SiC(Ti, B) films; (e) surface and (f) cross-section enlargements of SiC(Ti, B) films.

3.3. Effects of sintering additives on the physical properties of sintered SiC(Ti, B) films

3.3.1. Compositions and physical properties

Compositions and properties of sintered SiC(Ti, B) films presintered at 950 °C were studied due to their preferred microstructure, as shown in Table 1. Freestanding SiC(Ti, B) films of approximately 30 μm in thickness were selected to character their physical properties. This dimension suites for high temperature MEMS devices applications.[2,3,15] The results show that the room temperature elastic modulus and hardness of freestanding SiC(Ti, B) films with the density of 2.61 g cm^{-3} are 175 GPa and 7.8 GPa, respectively. The results of EPMA analysis indicate that oxygen content of the films is very low, since the oxygen has been removed as gaseous SiO and CO after pyrolysis at 1800 °C. The reason is that oxygen atoms exist in films mainly in the form of amorphous SiO_xC_y, which will decomposes with the evaporation of gaseous SiO and CO to form SiC at a temperature above 1000 °C.[26,27] And the gas will generate many flaws and cause mechanical property degradation. Therefore, it is worth noticing that the significantly lower oxygen content is benefit to high temperature resistance of freestanding SiC(Ti, B) films.

The results show that SiC(Ti, B) films have good mechanical properties and high density since sintering additives are effective for densification and retarding grain growth of SiC. The pyrolysis reaction of pure PCS may be described by the following reaction[37]:

$$\text{PCS(s)} \rightarrow \text{SiC(s)} + \text{C(s)} + \text{CH}_4\text{(g)} \qquad (1)$$

Table 1
Compositions and properties of continuous freestanding SiC(Ti, B) films.

	SiC(Ti, B) films
Film properties	
Thickness (μm)	32.36 ± 1.03
Density ($g\,cm^{-3}$)	2.61
Modulus (GPa)	175
Hardness (GPa)	7.80
Elemental composition	
Si (wt%)	65.63
C (wt%)	32.03
O (wt%)	1.65
Ti (wt%)	0.69
n(C)/n(Si)	1.139

When active TiN and B fillers were added to PCS, a series of reactions may occur during pyrolysis with various byproducts formed. For example, the fillers will react with the decomposition products of the polymer or a reactive gas during pyrolysis, the major reactions are[38–40]:

$$B(s) + CH_4(g) \rightarrow B_4C(s) + 2H_2(g) \quad (2)$$

$$B(s) + C(s) \rightarrow B_4C(s) \quad (3)$$

According to reactions (2) and (3), the weight loss decreases and the ceramic yield increases, the free carbon content decreases as the oxidation resistance of the derived ceramics occurs. Meanwhile, the in situ formation of excess carbide at the crystal boundary will suppress the growth of SiC crystals effectively. In contrast, an expansion to compensate for the polymer shrinkage is expected when reaction (4) prevails:

$$TiN(s) + B(s) \rightarrow TiB_2(s) + N_2(g) \quad (4)$$

Since the main product containing Ti after pyrolysis is TiB_2, it may be assumed that reaction (4) is the main reaction in the pyrolysis of SiC(Ti, B) films.

3.3.2. Heat-resistant performance

SiC(Ti, B) films and SiC films without sintering additives were exposed in argon for 1 h at 1500 °C, and their high temperature resistance were studied using SEM, XRD and hardness test. As shown in Fig. 5, the annealed films without sintering additives contain inter-connected and open porosity resulted from the release of CO, CO_2 in the thermal decomposition of SiC_xO_y above 1000 °C.[23,27] In contrast, the pores in the films modified by TiN, B sintering additives are much smaller and essentially closed, which might be attributed to the significantly lower oxygen content in the freestanding SiC(Ti, B) films.

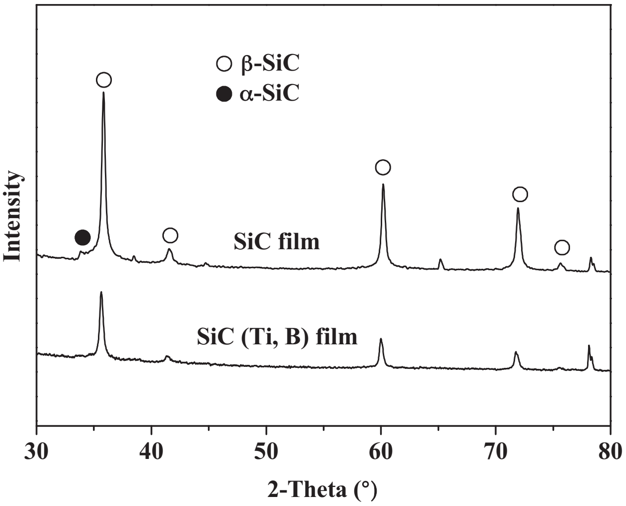

Fig. 6. XRD of SiC films and SiC(Ti, B) films annealed in Ar at 1500 °C for 1 h.

Fig. 6 depicts that the size of β-SiC crystals for the annealed films without sintering additives is much larger than that of SiC(Ti, B) films, which provides the fact that sintering additives are necessary to promote densification in sintering processes and effective for suppressing the growth of SiC crystals. The hardness of the annealed SiC(Ti, B) films is 7.3 GPa, which is much higher than the films without sintering additives (3.1 GPa). The results reveal that the heat-treated SiC(Ti, B) films retain good mechanical property, owing to the sintering additives which effectively suppress the growth of SiC crystals and decrease the oxygen content in the films.

In general, SiC(Ti, B) films with high modulus, high density and good high temperature resistance is competent for fabricating ultra-high temperatures MEMS, such as gear, pressure sensor membrane and combustion chamber in micro turbine engine. However, many important aspects in the correlation of microstructure with mechanical properties still need to be further explored. And MEMS processing technology also remains to be done and developed, SiC MEMS based on the fabrication technique of freestanding SiC(Ti, B) films would be realized by reactive ion etching and polymer-based bonding. For the polymer-based banding, a liquid precursor could be an adhesive layer to bond two or more SiC(Ti, B) films parts together. This technique thus could fabricate high aspect ratio MEMS structures, whose final thicknesses might not otherwise be achievable due to the size limitations with reactive ion etching.

4. Conclusions

In this investigation, freestanding SiC(Ti, B) films with high temperature resistance were synthesized from TiB-PCS precursor. Presintering process is identified to be the key factor to get densified films while the presintering temperature is related to the density of SiC seed crystals and content of B which can greatly affect the sintered microstructure of the films.

The sintered freestanding SiC(Ti, B) films with an average SiC crystal size of 35 nm are dense and uniform. Sintering additives are effective for suppressing the growth of SiC crystals and decreasing the oxygen and free carbon content, which are normally beneficial to high temperature resistance of films. The obtained results are expected to have important applications in MEMS for the environment of high temperature and such complex shaped-materials.

Acknowledgements

This work is supported by the Science and Technology Program of Fujian Province (Grant No. 2009H0038), the Fundamental Research Funds for the Central Universities (Grant No. 2010121053), the Aeronautical Science Foundation of China (Grant No. 2011ZF68004) and the Specialized Research Fund for the Doctoral Program of Higher Education (Grant No. 20110121120033).

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