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Effects of oxidation curing and Al atoms on the formation of near-stoichiometric freestanding SiC(Al) films derived from polyaluminocarbosilane (PACS)

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Abstract

The effects of oxygen pick-up and Al atoms on the formation and microstructure of freestanding SiC(Al) films by melt spinning of polyaluminocarbosilane (PACS) precursor were studied. PACS green films were cross-linked for 1 h, 2 h, 3 h and 4 h, pre-pyrolyzed at 900 °C, respectively. They were continuously pyrolyzed at 1800 °C to convert initial PACS into SiC(Al) ceramic films. Results reveal that the strict control of oxygen content during the oxidation curing is essential to produce near-stoichiometric SiC(Al) films. The microstructure of the dense films is a mixture of β-SiC crystals, α-SiC nano-crystals, C clusters and a small amount of Al_4O_4C and Al_4SiC_4. Al atoms which play important roles as both sintering aids and grain growth inhibitor are well distributed in the films due to the presence of stable composition and structure. SiC(Al) films with excellent mechanical properties would be attractive candidate materials for MEMS in harsh environments.

Keywords: Films; Curing; Microstructure-final; SiC; Microelectromechanical systems

1. Introduction

Si has been a dominant material for micromechanical components in microelectromechanical systems (MEMS) devices over approximately the past two decades. However, the inherent physicochemical properties that make Si attractive for MEMS restrict the applications including high temperature (over 500 °C), erosive, severe mechanical and chemical conditions.[1–4] SiC with a combination of unique physicochemical and mechanical properties, such as high strength, extreme hardness, as well as excellent resistance to wear, oxidation and corrosion is currently being investigated. These outstanding characteristics with respect to Si make SiC exceptionally well suit for power MEMS in harsh environments, the next generation of high-power, high-temperature electronic and optoelectronic devices applications.[5–9]

Preparation of MEMS for high-temperature applications is a two-fold problem: the first is selecting suitable refractory materials without the formation of voids and defects; the second is developing appropriate microfabrication techniques. Many papers have been published in recent years about making SiC based MEMS from liquid preceramic polymers.[10–16] These methods are suitable candidates to generate complex ceramic features applying soft lithographic techniques without the need for etching procedures. 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 cause extensive cracking and pore formation. Moreover, high temperature resistant of the above samples are also low, which will lead to invalidation of the corresponding devices at elevated temperatures. Therefore, the development of new materials and appropriate microfabrication techniques for high-temperature MEMS is of both scientific and practical interest to the MEMS community.

Our previous work has introduced a technique based on melt spinning of precursor to produce continuous freestanding SiC(Al) films which can avoid the significant difference of thermal expansion coefficient resulted from heteroepitaxial

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growth.[17] The fabrication progress has the main advantages of simple technology, low cost and good performance. However, the formation mechanisms of SiC(Al) films with dense structure are still unknown. And two fundamental questions relating the technique need to be answered. The first is how the oxygen picked up in the cross-linking of precursor would affect the formation and mechanical properties of SiC(Al) films. The second is how the Al atoms in the films would influence the microstructure of SiC(Al) films. Therefore, the aim of the present work is to prepare continuous freestanding SiC(Al) films with different oxidation curing time by melt spinning the polyaluminocarbosilane (PACS) precursor. The morphology, physical properties, microstructure and composition of the green and sintered films were characterized to provide a detailed understanding of technique and products. Effects of oxidation curing and Al atoms on the multiphase formation and structural evolution were also investigated.

2. Experimental procedure

PACS samples employed in this study were synthesized in our laboratory. They were prepared in an autoclave by thermolysis of a mixture of 4 g aluminum acetylacetonate [$Al(AcAc)_3$; Aldrich, 99%] with 100 g polysilacarbosilane (PSCS) at 450 °C under a N_2 atmosphere. Al element was introduced into the precursor PACS by cross-linking reaction in the formation of the Si–O–Al bonds during the process of synthesis. They are gold-colored solid with a number average molecular weight (M_n) of 2040 and a melting point of 300 °C.

The PACS was melt spun into green films using a melt spinning machine (MMCH05, Chemat, Northridge, CA) under 320 °C at an extrusion rate of 0.3 mm/min. Melting tank and cooling chamber in the machine were protected with high-purity nitrogen to prevent the precursor from oxidation. The thickness of green films greater than 100 m in length 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 (flow rate: 200 ml/min) with a heating rate of 3 °C/min and held for 1 h, 2 h, 3 h and 4 h at 180 °C, respectively. The cured PACS films were pre-pyrolyzed in an argon atmosphere (flow rate: 200 ml/min) with a heating rate of 5 °C/min and maintained for 1 h at 900 °C. The films were continuously pyrolyzed in an argon atmosphere (flow rate: 200 ml/min) with a heating rate of 40 °C/min up to 1800 °C.

These films with different amount of aluminum and oxygen were characterized by the following ways. The morphology of the films were observed using a scanning electron microscope (SEM) (Model 1530, LEO, Germany), their composition and microstructure were examined by electron probe microanalysis (EPMA) (JXA-8100, JEOL, Japan), Fourier transform infrared spectrometer (Nicolet Avatar FT-IR 360, USA), X-ray diffractometer (XRD) (X'pert PRO, Panalytical, Netherlands), Raman spectrometer (LabRam I, Dilor, France), X-ray photoelectron spectrometer (XPS) (PHI Quantum 2000, USA) and transmission electron microscope (TEM) (Tecnai F30, Philips-FEI, USA). The typical physical properties of films were tested by automatic bridge (HP16047A, USA), microhardness tester (HV-1000, Nboeo Detecting Instrument, China) and universal testing machine (Sun 2500, Galdabini, Italy).

3. Results and discussion

Fig. 1(a) shows the FTIR absorption spectra of PACS green films before and after curing for different time (bands at 2950 cm^{-1} and 2900 cm^{-1}, due to C–H stretching of Si–CH_3, at 2100 cm^{-1}, due to Si–H stretching, and at 1250 cm^{-1}, due to Si–CH_3 symmetric deformation). The broad and strong absorption with a maximum at about 1020 cm^{-1} induced by Si–C–Si stretching of Si–CH_2–Si in the cured films, enhances owing to the increase of Si–O–Si (band at 1080 cm^{-1}, due to Si–O stretching). The intense band at around 780 cm^{-1} is assigned to Si–CH_3 rocking and Si–C stretching.[18–21] The FTIRs exhibits that the adsorption peak of Si–H stretching at 2100 cm^{-1} of cured PACS films is evidently reduced compared with that of PACS green films, which are mainly resulted from the reaction of PACS with oxygen and formation of Si–O–Si bonds. It is worthy of noticing that the peaks become lower as cross-linking time increases. Moreover, the characteristic peak area ratios of 1020 cm^{-1} (the overlap of Si–C–Si stretching and Si–O stretching) to 780 cm^{-1} (Si–CH_3 rocking and Si–C stretching) for the samples increase with increasing cross-linking time also indicates a corresponding rise in the degree of Si–H reaction with oxygen.

Fig. 1(b) depicts the FTIR spectra of the films pyrolyzed at 900 °C, the Si–H peak at 2100 cm^{-1} disappears, and Si–CH_3 peak at 1250 cm^{-1} is shifted to a lower wavelength. It is revealed that the organic cured PACS are converted into SiC ceramic with the debonding of Si–H and Si–CH_3 during the pyrolysis reaction at 500–900 °C. The weaker adsorption peaks of C–H stretching of Si–CH_3 at 2950 cm^{-1}, 2900 cm^{-1} and Si–C–Si at 700–800 cm^{-1} can also prove that the C–H and Si–C bonds in the PACS are cleaved at about 900 °C. In addition, the FTIRs shows two asymmetric broad peaks of Si–O–Si stretching (1080 cm^{-1}) and Si–C stretching in SiC_4 (780 cm^{-1}), and the structures of both peaks change significantly. The peak of Si–O–Si shifts to higher wavenumber and the shape of the signal become broader with increasing cross-linking time. As a result of the decomposition of *SiOxCy* phase above 1000 °C,[22,23] the intensity of adsorption peak at 1080 cm^{-1} decreases with the rise of pyrolysis temperature, as shown in Fig. 1(c). One interesting phenomenon is that the peak intensity of the Si–C stretching vibration from the films cured for 3 h and sintered at 1800 °C is lower than that of films cured for 1 h, 2 h and 4 h.

The composition of freestanding SiC(Al) films after oxidation curing and pyrolysis is indicated in Table 1. Chemical concentrations were all measured by EPMA. As expected, it suggests an elemental composition (Si, C, O and Al) which is greatly changed by cross-linking time. All the films contain low amounts of Al and O. As the curing time rises, the Al and O contents increases, but the C content and C:Si ratio initially decrease and then slightly increase. The C:Si ratio of SiC(Al) films cured for 3 h, nearly stoichiometric composition, is calculated to be 1.03.