Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 41 (2015) 6898–6904
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Effect of deposition atmosphere on the phase composition and microstructure of silicon carbide films prepared by laser chemical vapour deposition

Ryuma Hashimoto, Akihiko Ito*, Takashi Goto

Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

Received 28 November 2014; received in revised form 13 January 2015; accepted 28 January 2015
Available online 4 February 2015

Abstract

β-SiC films were prepared by laser chemical vapour deposition using a Nd:YAG laser in a H_2 or Ar atmosphere. The effects of the deposition atmosphere on the film phase composition and microstructure were investigated. In a H_2 atmosphere, (111)-oriented β-SiC films consisting of submicron-sized grains were grown at 1273–1473 K, while carbon was codeposited with the β-SiC films grown at 1573–1673 K. In an Ar atmosphere, amorphous Si–C–O films were grown at 1073–1373 K, while (111)-oriented β-SiC films that did not contain free carbon were grown at 1473–1723 K. The deposition rates of the (111)-oriented β-SiC films were 1500–2000 μm h^{-1}.
© 2015 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: β-SiC; Laser chemical vapour deposition; High-speed deposition; Thick film

1. Introduction

Silicon carbide (SiC) shows promise as a protective material because of its excellent thermal shock and oxidisation resistances [1,2]. SiC coatings can be prepared by various techniques. For instance, chemical vapour deposition (CVD) is suitable for preparing high-purity, high-density, and conformal films at high deposition rates. Even though halide-based CVD is used extensively for the production of SiC films at relatively high deposition rates [3–5], this technique requires high deposition temperatures (greater than 1700 K) and generates hazardous chlorides as by-products.

Films of various oxides [6,7], carbides [8], and nitrides [9] have been prepared at high deposition rates (100–1000 μm h^{-1}) by laser CVD. β-SiC films have been grown on graphite substrates at a deposition rate of 2200 μm h^{-1} [8]. The high-speed epitaxial growth of (111)- and (110)-oriented β-SiC films has been achieved on (111) and (110) Si substrates, respectively [10].

Hexamethyldisilane (HMDS, $C_6H_{18}Si_2$) has been used widely as a SiC precursor during CVD because its vapour pressure at room temperature is moderately high and because it does not form hazardous and corrosive by-products. However, its carbon content is three times that of silicon and results in free carbon being present in the synthesised SiC films. Free carbon degrades the chemical, mechanical, and electrical properties of SiC but can be removed by adding either H_2 gas or an oxidant (i.e., O_2 and H_2O), which form hydrocarbons (e.g., CH_4) or carbonates (e.g., CO_2) in gaseous form, respectively. For instance, the addition of O_2 gas, which is a powerful oxidant of free carbon and may oxidise β-SiC to SiO_2, is easy and safe. On the other hand, in the case of laser CVD, the source gases are activated by laser irradiation. Therefore, trace amounts of O_2 in the common Ar gas (O_2 content less than 2 ppm) can eliminate the free carbon from the synthesised β-SiC films.

In the present study, SiC films were prepared by laser CVD in a H_2 or Ar atmosphere, and the effects of the deposition atmosphere on the film phase composition and microstructure were investigated.

*Corresponding author. Tel.: +81 22 215 2106; fax: +81 22 215 2107.
E-mail address: itonium@imr.tohoku.ac.jp (A. Ito).

http://dx.doi.org/10.1016/j.ceramint.2015.01.142
0272-8842/© 2015 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

2. Experimental

The laser CVD apparatus used has been described in detail elsewhere [11]. HMDS (LS-7120; Shin-Etsu Chemical, Japan) was evaporated at 293 K and its vapour was transported to the deposition chamber using H_2 or Ar as the carrier gas. The O_2 impurity level in the Ar gas was less than 2 ppm. The carrier gas was introduced into the chamber separately through a double-tube nozzle. The total pressure in the chamber was maintained at 800 Pa. The entire graphite substrate (10 mm in diameter and 1 mm in thickness) was irradiated with a continuous-wave Nd:YAG laser ($\lambda = 1064$ nm). The deposition temperature (T_{dep}) was measured using a pyrometer. T_{dep} was increased from 1073 to 1723 K by increasing the laser power from 60 to 245 W. The deposition rate was calculated using the film thickness and deposition time (0.6 ks).

The film phase compositions were determined through X-ray diffraction (XRD) analyses, which were performed using Cu Kα radiation (Rigaku, Ultima-IV; 40 kV and 40 mA). The cross-sectional microstructures of the synthesised films were observed with a scanning electron microscopy (SEM) system (Hitachi, S-3100H) and a transmission electron microscopy (TEM) system (Topcon, EM-002B). The binding energies of the C, Si, and O atoms were measured with X-ray photoelectron spectroscopy (XPS), which was performed using Al Kα radiation (Shimadzu-Kratos AXIS-ULTRA DLD). The spectra were fitted with a Gaussian function with baseline correction. The C–C peak at 284.8 eV was used as the charge reference.

3. Results and discussion

3.1. SiC films prepared in a H_2 atmosphere

Fig. 1 shows the XRD patterns of SiC films prepared at various T_{dep} in a H_2 atmosphere. Only peaks related to the graphite substrate were observed at 1173 K, implying that the corresponding film was amorphous (Fig. 1(a)). In the case of the film grown at 1273 K, a broad peak was observed at $2\theta = 36°$; this was indexed as belonging to 111 β-SiC (ICSD 24217) (Fig. 1(b)). A (111)-oriented β-SiC film was obtained at 1473 K (Fig. 1(c)). At 1673 K, carbon was codeposited with the synthesised (111)-oriented β-SiC film (Fig. 1(d)). The (0001) peak at $2\theta = 26°$ could be deconvoluted into two peaks, which were attributable to the deposited carbon ($2\theta = 25.5°$) and the graphite substrate ($2\theta = 26.4°$).

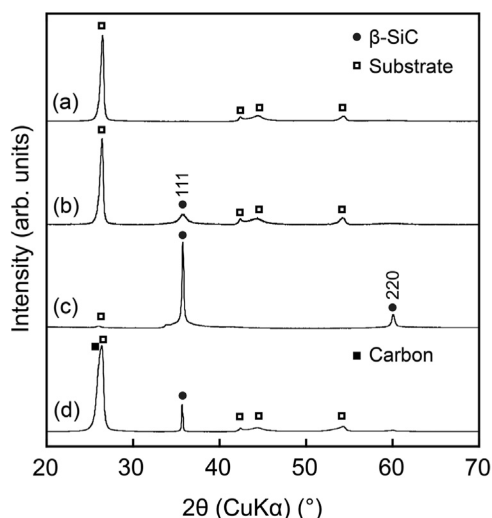

Fig. 1. XRD patterns of the SiC films prepared in a H_2 atmosphere at T_{dep} of (a) 1173 K, (b) 1273 K, (c) 1473 K, and (d) 1673 K.

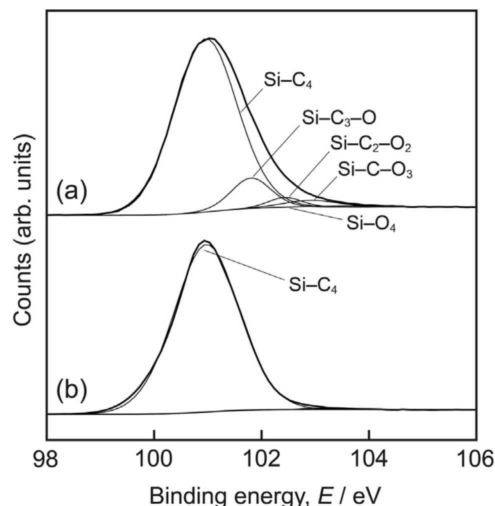

Fig. 2. Si 2*p* XPS spectra of the SiC films prepared in a H_2 atmosphere at T_{dep} of (a) 1173 K and (b) 1473 K.

Fig. 2 shows the Si 2*p* XPS spectra of SiC films prepared at various T_{dep} in a H_2 atmosphere. In the case of the film grown at 1173 K, the Si 2*p* peak could be deconvoluted into peaks related to $Si–C_4$, $Si–C_3–O$, $Si–C_2–O_2$, and $Si–C–O_3$ (Fig. 2(a)). The Si 2*p* binding energies in SiC ($Si–C_4$) and SiO_2 ($Si–O_4$) are 100–101 and 103–104 eV, respectively. The Si 2*p* peak observed at approximately 101 eV was associated with $Si–C_4$ (101.0 eV), $Si–C_3–O$ (101.8 eV), $Si–C_2–O_2$ (102.4 eV), $Si–C–O_3$ (102.9 eV), and $Si–O_4$ (103.6 eV) [12–15]. The C atoms in the $Si–C_4$ tetrahedron were partially substituted by an O atom. Therefore, the amorphous nature of the film prepared at 1173 K may explain the formation of the Si–C–O film. The presence of residual oxygen in the precursor furnace and the deposition chamber may account for the formation of Si–C–O. At 1473 K, the Si 2*p* peak became slightly sharper and almost fitted the spectrum of $Si–C_4$ at 101.0 eV (Fig. 2(b)).

Fig. 3 shows cross-sectional SEM and TEM images of the SiC films prepared at 1473 and 1673 K in a H_2 atmosphere. At 1473 K, the deposited SiC film consisted of fine grains (Fig. 3(a)). Further, the nanosized β-SiC particles formed a three-dimensional network (Fig. 3(b)). We estimated their grain size to be 98 nm using the Scherrer equation; this value was in agreement with the TEM observations. The selected-area electron diffraction (SAED) pattern showed a Debye–Scherrer ring, which was indexed as belonging to β-SiC (inset, Fig. 3(b)).

The β-SiC film prepared at 1673 K displayed a lamellar structure in the cross-sectional SEM and TEM images (Fig. 3(c) and (d)). The arc-like patterns and diffraction spots observed in its SAED pattern were attributable to carbon and β-

Download English Version:

https://daneshyari.com/en/article/1460424

Download Persian Version:

https://daneshyari.com/article/1460424

Daneshyari.com