



# SiC–SiO<sub>2</sub> nanocomposite films prepared by laser CVD using tetraethyl orthosilicate and acetylene as precursors

Shu Yu<sup>a,b</sup>, Rong Tu<sup>a</sup>, Akihiko Ito<sup>a,\*</sup>, Takashi Goto<sup>a</sup>

<sup>a</sup> Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

<sup>b</sup> State Key Laboratory for Powder Metallurgy, Central South University, Changsha, Hunan 410083, PR China

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## ABSTRACT

SiC–SiO<sub>2</sub> nanocomposite films were prepared by laser chemical vapor deposition (LCVD) using a CO<sub>2</sub> laser with tetraethyl orthosilicate (TEOS) and acetylene (C<sub>2</sub>H<sub>2</sub>) as precursors. The effects of laser power on the crystal phase and microstructure of the SiC–SiO<sub>2</sub> nanocomposite films were investigated. Films produced with laser power below 150 W (below 1523 K) had an amorphous structure, while those produced above 200 W (above 1673 K) were a mixture of crystalline SiC and amorphous phase. At 245 W (1774 K) the film contained 3C–SiC nanocrystals 100 to 200 nm in diameter dispersed in an amorphous matrix having high-density stacking faults formed on the (111) and (111) planes.

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## 1. Introduction

Nanocomposite films composed of nanocrystals (typically group IV elements: C, Si, Ge) dispersed in a SiO<sub>2</sub> matrix have unique luminescence and nonlinear optical properties [1–4]. SiC can be a suitable dispersoid candidate for nanocomposite film because of their high emissivity and wide band-gap; however, SiC–SiO<sub>2</sub> nanocomposite films have not been investigated in detail. First an amorphous Si–C–O film was prepared by sputtering, and then a nanocomposite film of SiC nanocrystals embedded in a SiO<sub>2</sub> matrix was obtained after post-annealing this amorphous film [5,6]. Although such films have been reported to exhibit photoluminescence, their microstructure is not well understood. Furthermore, the need for post-annealing could be a drawback for controlling the microstructure and improving their properties. Chemical vapor deposition (CVD) is a versatile technique for preparing nanocomposite films. However, SiC and SiO<sub>2</sub> are commonly thought to be thermodynamically incompatible because either SiC or SiO<sub>2</sub> will be stable depending on the oxygen potential. Therefore, chemical process like CVD will not be capable of preparing SiC–SiO<sub>2</sub> nanocomposite films. So far only physical vapor deposition (PVD) has been used to prepare SiC–SiO<sub>2</sub> nanocomposites.

In the present study, we describe the successful synthesis of a SiC–SiO<sub>2</sub> nanocomposite film with laser CVD, and report the effects of laser power on the crystal phase and microstructure of the SiC–SiO<sub>2</sub> nanocomposite films.

## 2. Experimental

Fig. 1 shows a schematic of the laser CVD apparatus. SiC–SiO<sub>2</sub> films were prepared in a cold-wall type CVD chamber on graphite discs (Sankyo Carbon Co., Ltd., IGS-743, 15 mm φ × 1 mm) using TEOS (tetraethyl orthosilicate; (C<sub>2</sub>H<sub>5</sub>O)<sub>4</sub>Si) and acetylene (C<sub>2</sub>H<sub>2</sub>) as precursors. TEOS was evaporated at 373 K and transported into the chamber with Ar gas. TEOS vapor and C<sub>2</sub>H<sub>2</sub> gas were introduced separately into the CVD chamber through a double-tube nozzle. Total pressure was fixed at 200 Pa. The graphite disc substrate was pre-heated on a heating stage to 823 K, and the continuous wave CO<sub>2</sub> laser (Symrad Inc. firestar f200; wavelength: 10.6 μm) was then introduced into the chamber through a ZnSe window, with an optical lens expanding the beam to about 20 mm in diameter so that the entire substrate is irradiated. The laser power was varied from 150 to 245 W, and the deposition temperature was measured by an infrared pyrometer (CHINO corp. IR-AH). The crystal phase was identified by X-ray diffraction (XRD; Rigaku RAD-2C). Microstructure was observed with a transmission electron microscope (TEM; JEOL JEM-2000FX). Photoluminescence spectrum was measured by a fluorescence spectrophotometer with xenon lamp at room temperature (PL; Hitachi F-4500; excitation wavelength: 270 nm).

## 3. Results and discussion

Fig. 2 shows the XRD patterns from SiC–SiO<sub>2</sub> films prepared at various laser powers between 150 and 245 W (corresponding to a deposition temperature between 1522 and 1774 K). A broad halo pattern around 2θ = 22° was observed below 150 W (below 1522 K) (Fig. 2(a)), indicating the film had an amorphous structure. When the

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

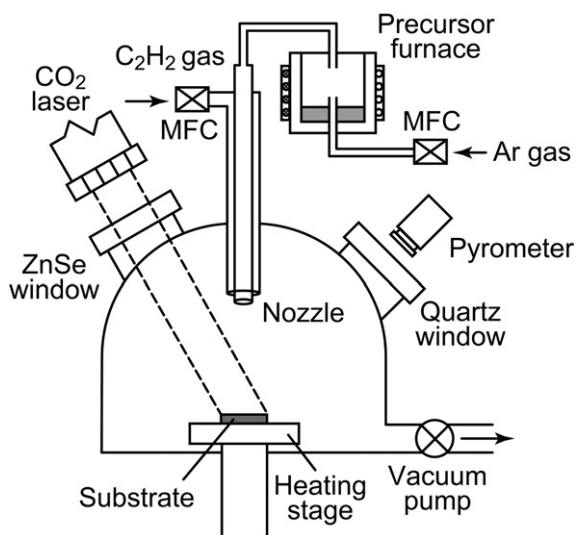


Fig. 1. A schematic of the laser CVD apparatus.

laser power was increased to above 200 W (above 1673 K), a  $\beta$ -SiC (3C-SiC) crystalline phase was co-deposited with the amorphous phase (Fig. 2(b)). The XRD peaks from 3C-SiC became stronger with increasing laser power and deposition temperature (Fig. 2(c)). An amorphous SiO<sub>2</sub> film is often obtained with CVD that uses a TEOS precursor [6,7], but so far no crystalline SiC phase has been reported from CVD using TEOS and C<sub>2</sub>H<sub>2</sub> as precursors. Nakayama et al. reported that Si–C–O (C-doped SiO<sub>x</sub>) films can be prepared with catalytic CVD using various metallic filaments (filament temperatures between 1572 and 2073 K) and using TEOS and DMDMOS (dimethyl-dimethoxysilane, Si(CH<sub>3</sub>)<sub>2</sub>(OCH<sub>3</sub>)<sub>2</sub>) as precursors [8,9]; however, no crystallographic or microstructural studies were conducted on the resulting films.

Fig. 3 shows bright-field TEM micrographs and a selected area of the electron diffraction (SAED) pattern from a SiC–SiO<sub>2</sub> nanocomposite film prepared at 1774 K. Nanosized crystalline grains 100 to 200 nm in diameter are dispersed in an amorphous matrix (Fig. 3(a)). As shown in Fig. 3(b), each nanocrystal has a fringe contrast. The SAED pattern from the nanocrystal shown in Fig 3(b) can be interpreted as

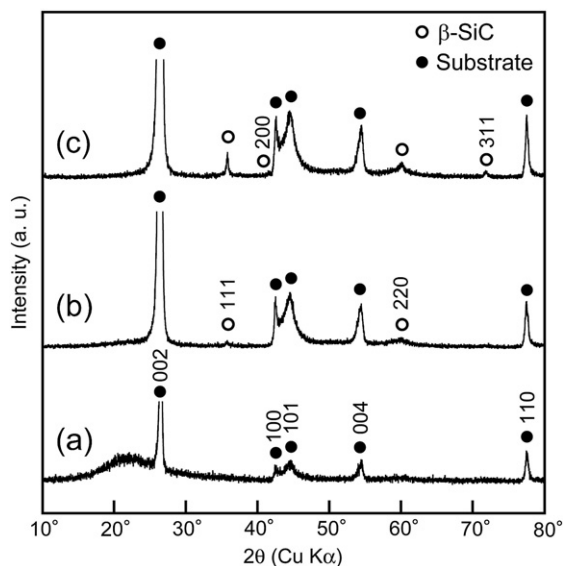


Fig. 2. XRD patterns of the SiC–SiO<sub>2</sub> films prepared on graphite substrates under 200 Pa at laser power of 150 W (deposition temperature of 1522 K) (a), 200 W (1673 K) (b) and 245 W (1774 K) (c).

the  $[\bar{1}10]$  and  $[1\bar{1}0]$  zone of the 3C-SiC structure (Fig. 3(c), (d)), suggesting that the 3C-SiC nanocrystal has a twinning structure with the twin boundary of the (111) plane. The continuous streaks in the SAED pattern along the  $[\bar{1}\bar{1}\bar{1}]$  and  $[11\bar{1}]$  directions imply that high-density stacking faults are formed on the  $(\bar{1}\bar{1}\bar{1})$  and  $(11\bar{1})$  planes. It is known that stacking faults of 3C-SiC crystals grown from vapor deposition always occur on the  $(\bar{1}\bar{1}\bar{1})$  and  $(11\bar{1})$  planes [10–12].

In 3C-SiC, the stacking faults form when the atomic order of the cubic closest packing structure changes, such as from ABCABC to ABCBABC. Because of the small difference in the free energy of formation among SiC polymorphs [13,14], stacking faults can be easily introduced during the crystal growth. Fig. 3(e) shows a schematic of the atomic arrangement inside the 3C-SiC nanocrystal. Only part of the bonds between the Si and C atom is depicted for simplicity. The SAED pattern indicates that the 3C-SiC nanocrystal has a twin boundary of the (111) plane, as shown by the line TB. The crystal planes of the two relatively large crystals across the twin boundary can be  $(1\bar{1}0)$  and  $(\bar{1}10)$  planes, and the twinning angle of 70.4° corresponds to an interplanar angle between the  $\{111\}$  planes. We also observed this interplanar relationship as a  $\Sigma 3$  coincidence boundary (indicated as  $\Sigma 3CB$ ). The continuous streaks along the  $[\bar{1}\bar{1}\bar{1}]$  and  $[11\bar{1}]$  directions in the SAED pattern indicate that the 3C-SiC nanocrystal grew along the  $[\bar{1}\bar{1}\bar{1}]$  and the  $[11\bar{1}]$  directions with a high density of stacking faults. The atomic arrangement illustrated by this schematic provides a good explanation for the fringe contrast and the facet shape that appears in the bright-field images.

Fig. 4 shows the PL spectrum of the SiC–SiO<sub>2</sub> films prepared at 1774 K. The PL spectrum can be fitted with a Gaussian function centered at 632 nm (dashed line in the Fig. 4). The defect structures of 3C-SiC including dislocations, stacking faults and twins have the luminescence band between 645 and 653 nm [15–17]. The intrinsic oxygen-excess defect in amorphous SiO<sub>2</sub> also exhibits the luminescence between 590 and 653 nm [18]. The observed spectrum corresponded to the emission from these defect centers.

#### 4. Conclusions

We prepared SiC–SiO<sub>2</sub> nanocomposite films by LCVD using TEOS and acetylene as precursors. Amorphous films were obtained at a laser power below 150 W (below 1523 K), while SiC–SiO<sub>2</sub> films were obtained at powers above 200 W (above 1673 K). Films produced at 245 W (1774 K) were found to consist of 3C-SiC nanocrystals 100 to 200 nm in size dispersed in an amorphous phase, and characterized by high-density stacking faults formed on the  $(\bar{1}\bar{1}\bar{1})$  and  $(11\bar{1})$  planes. The SiC–SiO<sub>2</sub> films prepared at 1774 K had photoluminescence centered at 632 nm.

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