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Preparation and characterization of a dual-layer carbon film on 6H-SiC wafer using carbide-derived carbon process with subsequent chemical vapor deposition☆

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ABSTRACT

It is reported that a dual-layer carbon film on SiC wafer is prepared using carbide-derived carbon (CDC) process with subsequent chemical vapor deposition (CVD). The dual-layer film includes a sub-layer of CDC and a top layer of CVD, which are prepared by chlorination of SiC and pyrolysis of CCl_4 at high temperature respectively. The CDC and CVD layers are mainly amorphous. And similar dispersion effects are observed in the Raman spectra, although the D-band position of the CVD layer shifts to higher wavenumber (~1354 cm^{-1}) than that of the CDC layer (~1337 cm^{-1}). Surface chemistry analysis suggests that the unstable chemical bonds, mainly C—Cl, as well as dangling bonds in the CDC layer play an important role in promoting the nucleation of CVD carbon. The surface morphology evolvement from SiC wafer to CDC layer and to dual-layer film is investigated by atomic force microscopy [AFM] and field emission scanning electronic microscopy [FESEM]. The nanoporous surface formed in the CDC process is favorable for capturing carbon species from the gas phase and can act as a "seedbed" for the nucleation and growth of CVD layer. The primary tribological study indicates that the dual-layer film shows great advantages in friction reduction and wear resistance with comparison to SiC and CDC layer, suggesting its potential in lubrication for SiC-based moving components.

1. Introduction

Because of their unique properties, such as high hardness, good corrosion resistance, and excellent chemical stability, SiC materials are widely used for tribological applications in extreme conditions [1]. However, the friction and wear coefficients of SiC materials are unacceptably high in unlubricated conditions [2]. To improve the tribological properties, carbon coatings such as diamond and diamond like carbon (DLC), are usually coated on such materials using chemical vapor deposition (CVD) process [3–5]. Although the CVD process is well established, the search for new methods for depositing carbon films continues. A promising method for coating carbon films on SiC termed the "carbide-derived carbon" or CDC process is greatly attractive in recent years [6]. In this method, SiC is treated in a chlorine-containing gas mixture at high temperature, and the Si atoms preferentially react with Cl_2 and leave the system in the form of $SiCl_4$ [7]. The left carbon atoms rearrange themselves and form a smooth carbon film that is intimately bonded to the underlying SiC substrate. Compared with CVD process, the CDC process can easily produce a thick carbon layer (above 100 um) at a high rate [6,7].

The CDC with unique nanostructure possesses many attractive physical, mechanical, and tribological properties. In particular, it is reported in recent studies that the CDC coating can afford very low friction and wear to improve the tribological performance of the carbides. Specifically, this coating can provide a friction coefficient of 0.03–0.3 and wear rate of 10^{-9}–10^{-7} $mm^3/N \cdot m$ depending on the chlorination process and friction test conditions [8–10]. Surprisingly, the CDC coating with high porosity (i.e.>57.2% for β-SiC [11]) shows excellent tribological properties under dry friction condition. However, unpublished studies in our group confirm that the CDC coating is helpless in lubricating for SiC materials under some conditions, including high temperature (i.e. at 300 °C), water or oil lubrication and high load. The lubrication failure is attributed to the high porosity and the low strength of CDC coating. Further surface modification to improve the density and strength of CDC coating is urgent for extensive tribology application. Although there is little pertinent research on such work to date, some information can still be obtained in some literature. Grannen and Chang [12] deposited diamond films from fluorocarbon gases in microwave plasma on SiC and WC substrates without any pretreatments. The proposed growth mechanism suggests that the surface carbon layer formed by the etching of carbide substrates with fluorine atomic favors the nucleation of diamond. It is reported that ultrananocrystalline diamond (UNCD) could also be deposited on the CDC films using microwave plasma CVD reactor and the tetrahedrally

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bonded carbon in the CDC films is suggested as a good seed for UNCD deposition [13].

Accordingly, we attempt to prepare a novel dual-layer carbon coating on 6H-SiC wafers using CDC technique with subsequent CVD process in the present work. According to our considerations, the CDC layer which is formed by chlorination of SiC acts as a seed and intermediate layer for subsequent deposition. The CVD process is operated in a same reactor using CCl_4 as carbon source. We used Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and field emission scanning electron microscopy (SEM) to determine the microstructure and chemistry of CDC and CVD films. And friction and wear properties of the CDC and dual-layer film are discussed. It is expected that this dual-layer film can provide better lubrication for SiC materials in many applications.

2. Experimental section

2.1. Film preparation

The dual-layer film was synthesized by pre-chlorination of single crystalline 6H-SiC wafer with subsequent chemical vapor deposition (CVD) using CCl_4 as precursor. The n-type 6H-SiC wafer (10×10 mm^2) with polished Si-face was purchased from TianKe Blue Semiconducter Co. Ltd (Beijing, China), with nominal cut-off angle of about 0–5°. The as-received SiC wafers were etched in dilute HF acid (40% solution) for 5 min to remove a SiO_2 layer, and ultrasonically cleaned in acetone bath for treatment. The schematic process to synthesize the dual-layer film was demonstrated in Fig. 1. Both the CDC process and CVD deposition were carried out in a tube furnace in turn. The CDC process was described in detail elsewhere [7]. In our experiments, the CDC layer was fabricated by chlorination of SiC in a gas mixture (Cl_2 at a flow speed of 2 ml min^{-1} + Ar at a flow speed of 98 ml min^{-1}) at 1000 °C for 10 min. The Si was preferred to react with Cl_2 and removed away in the form of volatile $SiCl_4$. The surface of SiC was converted into CDC and the shape of the sample stayed unchanged, as demonstrated in Fig. 1. Once the CDC process was finished, the Cl_2 flow was stopped immediately. Subsequently, the CCl_4 was evaporated at 60 °C [14] and introduced into reaction region with 50 ml min^{-1} Ar flow. The carbon derived from pyrolyzing of CCl_4 at 1000 °C nucleated and grew on top of CDC layer to form the CVD layer. The duration for CVD deposition was 2 h. The two principal chemical reactions taking place in the process included

$$SiC + 2Cl_2 \rightarrow SiCl_4 + C \quad (1)$$

which is thermodynamically allowed, with a Gibbs energy of $\Delta G = -434.1$ kJ/mol at 1000 °C, and

$$CCl_4 \rightarrow C + Cl_2 \quad (2)$$

which is also thermodynamically allowed, with a Gibbs energy of $\Delta G = -36.672$ kJ/mol at 1000 °C. The carbon produced by reaction (1) formed the CDC layer, while reaction (2) formed the CVD layer. As a result, the dual-layer carbon film composed of sub-layer of CDC and top layer of CVD carbon was synthesized. Moreover, single CDC film was also synthesized for comparison. The process parameters were the same to those in CDC process for dual-layer film preparation.

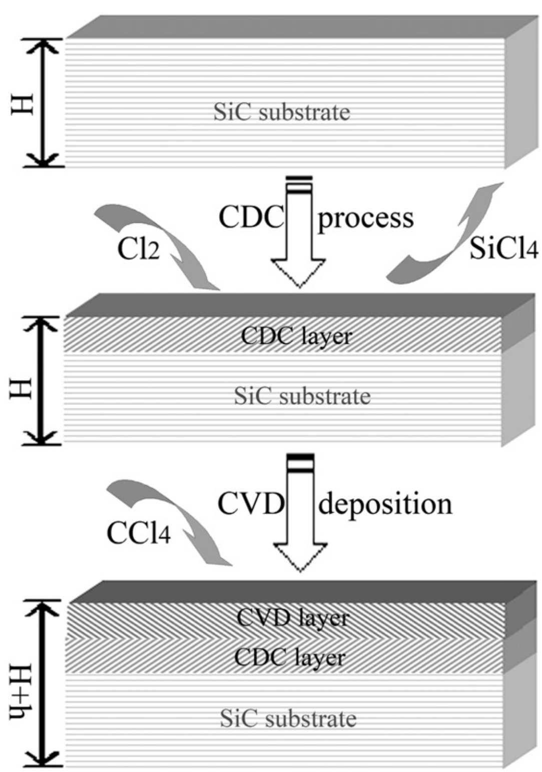

Fig. 1. Schematic fabrication process for the dual-layer carbon film. The processes were carried out in a silica tube furnace at 1000 °C. The surface of SiC was converted into CDC by etching in a chlorine-containing gas mixture. The shape of the sample stayed unchanged. The CVD layer was prepared by pyrolyzing CCl_4 on top surface of CDC layer and increased the sample thickness.

2.2. Characterization

Raman spectroscopy is a standard non-destructive analysis tool for characterization of various carbon materials. The CDC and the dual-layer films were studied on a Horiba HR800 Raman system with an Ar laser excitation wavelength of 532 nm. This system is also equipped with a charge couple device (CCD) detector and an optical imaging for focusing the laser at a micro-region. The Raman spectra were collected in the range between 600 and 2000 cm^{-1} for 60 s. X-ray photoelectron spectroscopy (XPS) was used to analyze the surface composition and chemical nature of the CDC layer and the dual-layer film. The XPS measurement was performed on PHI-5702 multifunctional photoelectron spectrometer, using Al–Ka X-ray (250 W) as the excitation source. No pre-treatment on the samples was conducted. Survey spectra with energy step of 0.4 eV and core level photoelectron lines C_{1s}, O_{1s}, Cl_{2p} and Si_{2p} with energy step of 0.125 eV were recorded. In order to investigate the surface topography evolvement, atomic force microscopy (AFM) was carried out with a Nanoscope IIIA Multimode apparatus (Veeco Instruments) under ambient conditions (relative humidity ~45%, temperature ~26–28 °C). AFM was performed in the tapping mode using rectangular silicon cantilevers with spring constant of ~40 Nm^{-1} and typical resonance frequencies between 250 and 300 kHz. Field emission scanning electronic microscopy (FESEM, JSM-6701F) was also employed to observe the surface microstructure.

2.3. Friction test

Friction and wear behaviors of SiC, CDC layer and dual-layer film were contrastively studied on a UMT-2MT tribo-meter (CETR, USA) with a ball-on-disk configuration in ambient conditions (temperature of 27 °C and relative humidity of 45%). The Si_3N_4 and steel balls with diameter of 3 mm made oscillating movement (5 mm in amplitude) on the top of the samples for 30 min. The test conditions were 1 N in load and 20 mm s^{-1} in sliding speed. The friction coefficients were recorded by the tribo-meter.