Diamond & Related Materials 18 (2009) 1426–1434

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

The effect of the CH_4 level on the morphology, microstructure, phase purity and electrochemical properties of carbon films deposited by microwave-assisted CVD from Ar-rich source gas mixtures

Yoshiyuki Show [1], Vernon M. Swope, Greg M. Swain *

Department of Chemistry and the Fraunhofer Center for Coatings and Laser Applications, Michigan State University, East Lansing, MI 48824-1322, United States

A R T I C L E   I N F O

Article history:
Received 8 May 2008
Received in revised form 24 August 2009
Accepted 25 September 2009
Available online 2 October 2009

Keywords:
Nanocrystalline diamond
Film morphology and microstructure
Electrochemistry

A B S T R A C T

Carbon thin films were deposited on Si substrates by microwave-assisted chemical vapor deposition (CVD) using variable CH_4 levels in an Ar/H_2 (Ar-rich) source gas mixture. The relationship between the CH_4 concentration (0.5 to 3 vol.%) in the source gas and the resulting film morphology, microstructure, phase purity and electrochemical behavior was investigated. The H_2 level was maintained constant at 5% while the Ar level ranged from 92 to 94.5%. The films used in the electrochemical measurements were boron-doped with 2 ppm B_2H_6 while those used in the structural studies were undoped. Boron doping at this level had no detectable effect on the film morphology or microstructure. Relatively smooth ultrananocrystalline diamond (UNCD) thin films, with a nominal grain size of *ca.* 15 nm, were only formed at a CH_4 concentration of 1%. At the lower CH_4 concentration (0.5%), faceted microcrystalline diamond was the predominant phase formed with a grain size of *ca.* 0.5 µm. At the higher CH_4 concentration (2%), a diamond-like carbon film was produced with mixture of sp^2-bonded carbon and UNCD. Finally, the film grown with 3% CH_4 was essentially nanocrystalline graphite. The characteristic voltammetric features of high quality diamond (low and featureless voltammetric background current, wide potential window, and weak molecular adsorption) were observed for the film grown with 1% CH_4, not the films' grown with higher CH_4 levels. The C_2 dimer level in the source gas was monitored using the Swan band optical emission intensity at 516 nm. The emission intensity and the film growth rate both increased with the CH_4 concentration in the source gas, consistent with the dimer being involved in the film growth. Importantly, C_2 appears to be involved in the growth of the different carbon microstructures including microcrystalline and ultrananocrystalline diamond, amorphous or diamond-like carbon, and nanocrystalline graphite. In summary, the morphology, microstructure, phase purity and electrochemical properties of the carbon films formed varied significantly over a narrow range of CH_4 concentrations in the Ar-rich source gas. The results have important implications for the formation of UNCD from Ar-rich source gas mixtures, and its application in electrochemistry. Characterization data by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), visible-Raman spectroscopy and electrochemical methods are presented.

1. Introduction

Our group is developing high surface area and electrically conducting diamond materials for use as a dimensionally stable electrocatalyst support [1–6]. The approach to making these powders involves CVD overcoating of diamond abrasive powders as well as various sp^2 carbon materials with a thin layer of boron-doped ultrananocrystalline diamond (B-UNCD) grown from a $CH_4/H_2/Ar/B_2H_6$ source gas mixture (Ar-rich) [1–6]. Advanced electrocatalyst supports are needed for polymer electrolyte membrane fuel cells (PEMFCs) because currently used sp^2-bonded materials (e.g., carbon blacks) undergo degradation and corrosion during extended operation and automotive cycling [7]. Any advanced electrocatalyst support should possess high surface area (>100 m^2/g) and high electrical conductivity (>0.5 S/cm). These diamond-coated powders are microstructurally stable and corrosion resistant during anodic polarization (*e.g.,* 1.4 V vs. RHE in 0.5 M H_2SO_4 at 80 °C) and they provide good electronic coupling with the nanometer-sized metallic electrocatalyst particles. Electrically conducting diamond powders are also useful as a stationary phase for electrochemically-modulated liquid chromatography [8]. The ideal form of diamond for these small, irregularly-shaped substrates appears to be UNCD, although the larger sized powder particles can be coated with diamond deposited from conventional CH_4/H_2 source gas mixtures [1–6]. The UNCD used by our group is typically deposited from a 1% CH_4/5% H_2/94% Ar source gas mixture with 10 ppm B_2H_6 added for boron doping [3–6,9–12]. The structure and properties of UNCD grown from Ar-rich source gas

---

* Corresponding author. Tel.: +1 517 355 9715x229; fax: +1 517 353 1793.
E-mail address: swain@chemistry.msu.edu (G.M. Swain).

[1] Present address: Faculty of Engineering, Tokai University, Hiratsuka, Japan.

0925-9635/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2009.09.011

mixtures have been reported on extensively [13–25]. Importantly, the electrochemical properties of B-UNCD films have been observed to be similar to those of boron-doped nanocrystalline diamond films deposited from traditional CH_4/H_2 source gas mixtures [9].

Diamond deposition on the powders is accomplished by microwave-plasma CVD with the sample spread as thinly and evenly as possible across a Si substrate [1–6]. While this approach yields a high fraction of coated particles, there are some technical limitations that remain to be overcome. First, diamond growth does not occur exclusively over individual particles but rather over multiple neighboring particles "connecting" them together; a process that reduces the specific surface area of the material. Second, reactive gas species are not fully accessible to all of the particle surfaces either because of blockade by contact with the Si substrate or burial by other particles within the sample. This leads to partial diamond overlayer coverage. Third, in our microwave reactor design, the substrate particles are not independently heated but rather are heated by collisions with plasma species and the exothermic H atom recombination reaction that occurs on the surface. Therefore, the substrate temperature is controlled by both the microwave power and system pressure. Because there is variable particle height in the plasma, a powder sample will not be at constant temperature during deposition. For example, the temperature will be higher than targeted at a group of particles projecting up into the plasma. Conversely, the temperature will be lower at a group of particles buried within the sample. In part, because of this temperature variation, we observe a couple of different carbon microstructures when overcoating small diameter (3–100 nm) diamond or sp^2 carbon powder particles with UNCD grown from 1% CH_4/5% H_2/94% Ar + 10 ppm B_2H_6. These microstructures are the predominant small-grained UNCD phase and platelet-like, nanocrystalline graphite [5]. We suppose that these different microstructures also form because of variable reactive carbon levels within a powder sample due to hindered mass transfer from the gas phase or increases in the local reactive carbon concentration due to substrate gasification by the atomic hydrogen in the plasma.

In order to better understand the relationship between the reactive carbon level and the film morphology and microstructure, we investigated the structure of thin carbon films deposited from $CH_4/H_2/Ar$ (Ar-rich) source gas mixtures with varying levels of CH_4 from 0.5 to 3%. The films were grown on Si substrates, which allowed for easy characterization of the physicochemical properties. Compositional mapping has been reported for nanocrystalline and ultrananocrystalline diamond films deposited using both microwave-plasma and hot-filament CVD [13,26–29]. In all but one of these studies, the CH_4 level was fixed and the H_2 and/or Ar levels were varied. For example, Zhou *et al.* studied the growth of diamond films as a function of the Ar level in CH_4/H_2 microwave plasma [13]. In another report, Jiao *et al.* studied the nucleation and growth of nanocrystalline diamond films grown from CH_4/Ar source gas mixtures with and without added H_2 [27]. Lin *et al.* mapped how the $CH_4/Ar/H_2$ source gas composition in hot-filament CVD influences the diamond film microstructure and morphology [26]. Nanocrystalline diamond was formed at Ar levels above 96% and CH_4/H_2 levels between 2 and 6%. More recently, Azevedo *et al.* reported on the morphology and microstructure of nanocrystalline diamond films deposited with variable CH_4 levels (0.5 to 3.5%) using hot-filament CVD, while keeping the Ar concentration constant at 90% [29]. The balance of the source gas was H_2, which ranged from 6.5 to 9.5%. They found that diamond was formed at CH_4 levels at or below 2%. Above 2%, there was a gradual transition from diamond to graphite. In general, for microwave CVD, variation of source gases containing 1% CH_4 and no Ar (H_2 rich) to source gases containing 1% CH_4 and no H_2 (Ar-rich) produces a fundamental change in the plasma chemistry, growth mechanism, growth rate and film structure.

We report herein on the microwave-plasma CVD growth and characterization of thin films of carbon deposited from Ar-rich source gas mixtures. The CH_4 level was varied from 0.5 to 3%, while the H_2 level was held constant at 5%. The balance of the source gas was Ar, which ranged from 92 to 94.5%. The films used in the electrochemical measurements, were deposited using similar conditions but with 2 ppm of B_2H_6 added for boron doping. Variations in the CH_4 level over this narrow compositional range produces a progressive transition in film structure from microcrystalline diamond at 0.5%, UNCD at 1%, diamond-like carbon at 2%, and nanocrystalline graphite at 3%. The film morphology, crystallinity, microstructure and electrochemical properties were strongly affected by the changes in CH_4 concentration in these Ar-rich mixtures. The C_2 dimer level present in the plasma was qualitatively assessed from the Swan band optical emission at 516 nm [13]. It was found that both the growth rate and the dimer emission intensity increased with the CH_4 concentration in the source gas. Therefore, the C_2 dimer appears to be involved in the growth of both types of diamond as well as the diamond-like carbon and nanocrystalline graphite. Characterization data from scanning electron microscopy (SEM), a transmission electron microscopy (TEM), X-ray diffraction, Raman spectroscopy, and electrochemical measurements are reported.

2. Experimental

2.1. Carbon film growth

The carbon films were deposited on 1 cm^2 *p-type* Si(100) (~10^{-3} ohm-cm, Virginia Semiconductor Inc., Fredericksburg, VA) using a commercial microwave plasma CVD system (1.5 kW, formerly ASTeX, Inc., Lowell, MA). The substrate was prepared by mechanically scratching the surface with 0.1 μm diameter diamond powder (GE Superabrasives, Worthington, OH) for 5 min on a felt polishing pad. The uniformly scratched substrate was then sequentially washed with ultrapure water, isopropyl alcohol (IPA), acetone, IPA, and ultrapure water. This was followed by extensive ultrasonic cleaning in acetone to remove all polishing debris from the surface. This treatment produces a high number of clean scratches and embedded diamond particles, both of which serve as the initial nucleation sites during film growth.

Ultrahigh purity (99.999%) CH_4, Ar and H_2 were used in the source gas. The total gas flow rate was maintained at 100 sccm and the gases were mixed prior to entering the reaction chamber. The CH_4 level was varied from 0.5 to 3% by appropriate adjustment of the flow rate, as indicated in Table 1. The H_2 level was maintained constant at 5%. As mentioned, the addition of some H_2 was necessary in order to stabilize the plasma in our CVD reactor. The balance of the source gas was made up of Ar at flow rates from 92 to 94.5%. The microwave power and deposition pressure were 800 W and 18.6 kPa (140 Torr), respectively. The nominal substrate temperature was estimated by optical pyrometry to be near 750 °C. The deposition time for films deposited with CH_4 levels up to 2% was 2 h, while the deposition time for the 3% CH_4 film was only 15 min. The film thicknesses ranged from 2–14 μm (see Table 1).

The films used in the electrochemical measurements were grown under the same conditions but with ultrahigh purity B_2H_6 (0.1% in H_2) added (2 ppm) for boron doping [4–9,11,12]. The same *p-type* Si(100)

Table 1
Source gas compositions and growth times for the carbon films formed with different CH_4 concentrations in the Ar/H_2 source gas.

CH_4 (%)	CH_4 flow (sccm)	Ar flow (sccm)	H_2 flow (sccm)	Growth time (h)
0.5	0.5	94.5	5	2
1.0	1	94	5	2
2.0	2	93	5	2
3.0	3	92	5	0.25

The film thicknesses were *ca.* 2, 5, 13 and 2 μm, respectively, for the films deposited from 0.5, 1, 2 and 3% CH_4.