Available online at www.sciencedirect.com
SCIENCE DIRECT
Thin Solid Films 494 (2006) 110 – 115
thin solid films
www.elsevier.com/locate/tsf

Plasma-enhanced synthesis of diamond nanocone films

Q. Yang [a,*], T. Hamilton [b], C. Xiao [b], A. Hirose [b], A. Moewes [b]

[a] Department of Mechanical Engineering, University of Saskatchewan, 57 Campus Drive, Saskatoon, SK, Canada S7N 5A9
[b] Department of Physics and Engineering Physics, University of Saskatchewan, 116 Science Place, Saskatoon, SK, Canada S7N 5E2

Available online 24 August 2005

Abstract

Three DC plasma processes in a hot filament reactor were developed to synthesize nanostructured carbon films: (1) pure hydrogen plasma treatment of diamond films pre-coated on silicon substrate, (2) plasma-enhanced hot filament chemical vapor deposition (HFCVD) with a gas mixture of hydrogen and methane and (3) graphite etching in a pure hydrogen plasma. Highly aligned diamond nanocone films were synthesized on silicon substrates pre-coated with diamond films in all three processes. When the silicon substrates were pre-deposited with sparsely distributed diamond particles, diamond and graphitic nanocones were grown simultaneously on substrate areas with and without pre-deposited diamond particles, respectively in the last two processes. All the nanocones have nanometer-size tips and sub micrometer-size roots and are highly aligned with various orientation angles influenced by the direction of the electric field lines near the sample surface. In comparison with the conventional method using a methane and hydrogen mixture, it is found that diamond nanocones synthesized by graphite etching have one order of magnitude higher cone density, lower sp^2 carbon content and grow four times faster.

Keywords: Plasma processing and deposition; Diamond nanocone films; Nanostructures; Chemical vapor deposition

1. Introduction

Diamond has many superior properties, such as extreme hardness, high transparency, high thermal conductivity, high chemical stability and negative electron affinity (NEA). Beside various industrial applications already developed, such as heat sinks, abrasives and cutting tools, its applications in electronics are also promising. Diamond is considered an excellent cold cathode material suitable for various applications including electron sources, flat panel displays and a new generation of microwave tubes. In the past decade, field electron emission (FEE) from diamond and carbon nanostructures has attracted considerable interest [1–6]. It has been found that carbon nanotubes and nanofibers exhibit lower turn-on electric field due to its high geometrical enhancement factor (GEF) near the tips [6]. Nanocones with nanometer-sized tips and sub micrometer-sized roots are expected to have GEF similar to that of nanotubes and nanofibers. The main advantage of nanocones is their larger rigidity compared to nanotubes or nanofibers. Rigidity and sub micrometer-sized roots allow for fabrication of emitter arrays and for an extended lifetime of the emitters. Due to the NEA of diamond and high GEF of nanocones, well aligned diamond nanocone films are expected to exhibit better field emission properties than conventional smooth diamond thin films or other carbon nanostructures.

Diamond and diamond-like carbon nanocones have recently been synthesized using microwave plasma-enhanced chemical vapor deposition (MPCVD) [7–9]. Our recent work [10,11] has demonstrated that graphitic and diamond nanocone films can be synthesized by HFCVD. In this paper we further show that well aligned diamond nanocone films can be synthesized through three different plasma processes in a HFCVD reactor, and mixed graphitic and diamond nanocone films can be simultaneously synthesized on the same substrate.

* Corresponding author. Tel.: +1 306 966 5470; fax: +1 306 966 5427.
E-mail address: qiy866@mail.usask.ca (Q. Yang).

0040-6090/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2005.07.181

2. Experimental methods

An HFCVD system described elsewhere [12] was used to synthesize diamond nanocones. The filament was a coiled tungsten wire of 0.3 mm in diameter and was heated by an AC power supply at a voltage of 30~40 V and current of 8 to 10 A. A thermocouple was mounted right behind the substrate to measure the substrate temperature. The substrate temperature was between 650 °C and 750 °C (typically 700 °C). The distance between filament and substrate was typically 8 mm. P-type (100)-oriented mirror polished Si wafers were used as substrates. The substrate was either coated with a diamond film of 7~10 μm, or deposited with sparsely distributed diamond particles in the same HFCVD device without plasma. After the substrate was mounted onto the substrate holder, the deposition chamber was pumped down to a base pressure of 2.7 Pa using a rotary pump. Reaction gases were introduced using mass flow controllers. Hydrogen flow was kept constant at a rate of 35 sccm. When the working pressure was stabilized at the preset values in the range of 5.32 Pa to 1.97 kPa (typically 1.04 kPa), a current was passed through the tungsten filament coil. A DC glow discharge was initiated between substrate holder (as cathode) and filament. The discharge voltage between filament and substrate was in the range of 300 V to 550 V (typically 350 V) and the corresponding substrate current was between 50 mA and 150 mA (typically 100 mA). The processing time was between 1.5 h and 3 h. Experimental set-up and plasma discharge conditions were the same for all the plasma processes described below (unless otherwise indicated) and different gases were used in the three different synthesis processes.

Three plasma processes were used to synthesize diamond nanocone films in the hot filament reactor: (1) hydrogen plasma treatment of the diamond films pre-coated on the silicon substrate, (2) plasma-enhanced HFCVD using a gas mixture and (3) graphite etching in a hydrogen plasma. In the first process, pure hydrogen plasma (without any carbon source in the system) was used. The pre-coated diamond films were anisotropically etched by the hydrogen plasma. In the second process, conventional HFCVD with a gas mixture of hydrogen and methane (0.5~1.5 vol.%, typically 1 vol.%) was used. In the third process, pure hydrogen was introduced and an isotropic ultra fine polycrystalline graphite sheet (Poco's EDM-3) was placed beneath the silicon substrate. In this case the graphite etched in situ by hydrogen acts as the carbon source for diamond growth. The synthesis parameters of the three plasma processes are summarized in Table 1.

The deposited films were analyzed by scanning electron microcopy (SEM), Micro-Raman spectroscopy and soft X-ray absorption spectroscopy (XAS). The XAS measurements were performed at Beamline 8.0.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory. The Raman spectra were obtained using a Renishaw Micro-Raman System 2000 Spectrometer operated at the argon laser wavelength of 514.5 nm. The laser spot size was approximately 1 μm with a power of 20 mW.

3. Results and discussion

Fig. 1 shows typical SEM micrographs of the films synthesized on diamond films pre-coated on Si substrate for the three synthesis procedures. Highly aligned nanocone

Table 1
Synthesis parameters and characterization results of diamond nanocones using three different plasma processes

Parameter	Variation range	Typical value	
Filament voltage	30~40 V	36 V	
Filament current	8~10 A	9.3 A	
Substrate temperature	650~750 °C	700 °C	
Substrate	Si coated with diamond film or particles	7~10 μm film	
Working pressure	5.32 Pa~1.97 kPa	1.04 kPa	
Substrate bias voltage	−300~−550 V	−350 V	
Discharge current	50~150 mA	100 mA	
Total gas flow rate	35 sccm		
Processing time	1.5~3 h		
	Plasma treatment	CVD with the gas mixture	Graphite etching
Gas mixture	Hydrogen	Hydrogen and methane (0.5~1.5 vol.%, typically, 1 vol.%)	Hydrogen
Carbon source for growth	Through etching pre-coated diamond	Methane	In situ etched graphite
Cone length (μm) per hour	0.4	0.4	2
Average growth rate, μm/h	Through etching	0.4	2
Cone density, cm^{-2}	$\sim 10^8$	$\sim 10^8$	$\sim 10^9$
Relative concentration of sp^2 from XAS and Raman measurement	Lower than that by graphite etching	Low	Lower than that by CVD with the gas mixture