Available online at www.sciencedirect.com
SCIENCE DIRECT
Diamond & Related Materials 15 (2006) 1336 – 1349
DIAMOND AND RELATED MATERIALS
www.elsevier.com/locate/diamond

Low surface temperature synthesis and characterization of diamond thin films

D. Das, V. Jayaseelan, R. Ramamurti, R.S. Kukreja, L. Guo, R.N. Singh *

Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH 45219, United States

Received 12 July 2005; received in revised form 22 September 2005; accepted 10 October 2005
Available online 28 November 2005

Abstract

Polycrystalline diamond films are deposited on p-type Si(100) and n-type SiC(6H) substrates at low surface deposition temperatures of 370–530 °C using a microwave plasma enhanced chemical vapor deposition (MPECVD) system. The surface temperature during deposition is monitored by an IR pyrometer capable of measuring temperature between 250 and 600 °C in a microwave environment. The lower deposition temperature is achieved by using an especially designed cooling stage. The influence of the deposition conditions on the growth rate and structure of the diamond film is investigated. A very high growth rate up to 1.3 μm/h on SiC substrate at 530 °C surface temperature is attributed to an optimized Ar-rich $Ar/H_2/CH_4$ gas composition, deposition pressure, and microwave power. The structure and microstructure of the films are characterized by X-ray diffraction, scanning electron microscopy, and Raman spectroscopy. A detailed stress analysis of the deposited diamond films of grain sizes between 2 and 7 μm showed a net tensile residual stress and predominantly sp^3-bonded carbon in the deposited films.

Keywords: Polycrystalline diamond; Low temperature deposition; Surface temperature; Tensile stress; Silicon; Silicon carbide

1. Introduction

The diamond film research has attracted renewed interest in recent years because of its outstanding optical, electrical, mechanical, and thermal properties [1]. However, the high temperatures (800–900 °C) normally employed in fabricating chemical vapor deposited (CVD) diamond films limits the application to predominantly high melting semiconductor materials. Deposition of diamond film over a large substrate area and at lower temperatures is also useful for many industrial applications including electronics. In particular, the deposition of diamond films at lower surface temperatures has applications in thermal management of electronic devices operated at high powers and frequencies. Since the majority of these high power and high frequency electronic and optoelectronic devices are based on Si or SiC, the deposition of diamond films at low temperatures and their thermal conductivity on these substrates are important topics of this investigation. The thermal property investigation of diamond films is underway and will be communicated separately.

Fabrication of the CVD diamond films at lower substrate temperatures has been done by using different pre-treatment of the substrate for the nucleation step, precursor gases or processing conditions than those used in the conventional CVD processes [2–23]. Nanodiamond seeding of the substrates has been found beneficial in achieving low temperature (T_{sub}=200 °C) diamond growth on Si substrates with very high particle density [2–5]. Halogenated (especially F_2 and Cl_2) precursors have been used to synthesize CVD diamond at low substrate temperatures (T_{sub}=370 °C) [6–9]. The ease of formation of the hydrocarbon radicals from the halogenated precursor accelerated the diamond growth. But, at lower temperature, the lack of etching of the graphitic phases by halogenated precursors seriously deteriorated the diamond film quality. Oxygen containing precursors (CO/H_2, $CO/H_2/O_2$, or CO_2/CH_4), on the other hand, improved the film quality as well as helped in achieving low temperature (T_{sub}=130 °C) CVD diamond film growth [10–13]. Carbon monoxide-rich CO/H_2 mixture was able to produce low temperature diamond film with very high growth rate of 2.5 μm/h. Addition of a small amount of O_2 to the conventionally used CH_4/H_2 gas mixture helped in achieving diamond film growth on borosilicate glass, fused silica, and on Si at lower substrate temperatures in hot

* Corresponding author. Tel.: +1 513 556 5172; fax: +1 513 556 3773.
E-mail address: Raj.Singh@uc.edu (R.N. Singh).

0925-9635/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2005.10.016

filament assisted CVD (HFCVD) [14]. Using HFCVD diamond deposition on Si surfaces was performed even at 135 °C by cooling the substrate by a stream of water flowing around the substrate holder [15]. More recently, camphor has been used as the precursor material in realizing diamond growth at low temperatures [16]. Argon-rich Ar/CH_4 plasma was found beneficial in producing ultrananocrystalline diamond film at low substrate temperatures [17]. Magneto-active microwave plasma or electron cyclotron resonance plasma assisted CVD (ECR-CVD) has been employed to deposit diamond over a larger substrate area at lower temperatures and pressures (less than 1 Torr) [18–21]. Low substrate temperature was also achieved by pulsing the microwave plasma or magneto-active microwave plasma in fabricating CVD diamond film [22,23].

Although the low temperature deposition reduces the large thermal stresses in the film compared to their high temperature counterpart (due to large thermal expansion mismatch between Si and diamond), non-diamond impurities and defects incorporation into the deposited film can be an obvious problem in low temperature diamond growth (LTDG). Stiegler et al. have studied the microstructural evolution and structural defects in the diamond film deposited at low substrate temperatures [24–26].

The real deposition temperature was not mentioned in most of the literatures on the LTDG. The diamond surface temperature during deposition was rarely monitored and expected to be significantly different (higher) than the substrate temperature monitored from underneath because of the difference in emissivity of diamond and Si substrate, thermal gradient, and methods used to monitor the temperature. Most literatures do not describe the temperature measurement procedures for the low temperature experiments [12,16]. Some researchers have measured the temperature of the substrate holder by inserting a thermocouple through a drilled hole in the substrate holder stage [13,14]. Others reported use of a thermocouple clamped to the side of the substrate or attached to the topside of the substrate directly below the filament (in case of the hot filament assisted chemical vapor deposition) [8,9]. In some cases, to calibrate the thermocouple inserted into the substrate holder, a second thermocouple was mounted either on the substrate surface or in between the substrate and the holder by means of a metallic indium [10,11,15]. To measure the substrate surface temperature, thermocouple was directly mounted on the substrate surface by means of a glue [2,4]. However, in all these investigations, the temperature of the growing diamond surface on the substrate was not known. The temperature measured either by a single thermocouple inserted through a drilled hole in the substrate holder stage or by calibrating the inserted thermocouple by placing a second thermocouple on the substrate surface cannot measure the true surface temperature. The temperature measured by the thermocouple placed on the substrate surface is also erroneous, because the thermocouple tip interferes with the plasma and gets heated by itself. Although Stiegler et al. measured the substrate surface temperature by means of an IR pyrometer operated at a wavelength of approximately 8 μm (to exclude any interference from plasma emission) directed towards the surface [24,25], they have not mentioned the window materials used in their measurements. Ordinary fused quartz or silica will absorb most of the radiations at that wavelength and the real surface temperature will be much higher than the reported temperature. Schmidt and Benndorf measured the surface temperature by means of both IR pyrometer and several NiCr/Ni thermocouples [6,7] but the pyrometer's working range was not specified.

The primary objective of this study is to investigate the effect of the surface temperature of the substrate on the low temperature diamond growth on Si and SiC substrates at temperatures between 370 and 530 °C in an MPECVD system. The surface temperature measurement has been possible because of the use of a special IR pyrometer operating at a wavelength between 2 and 2.6 μm for surface temperature measurement between 250 and 600 °C, which also works in a microwave environment. The control of the surface deposition temperature was achieved by using a sample holder with provisions for cooling the substrate, and by control of the microwave power, circulating cooling water flow rate, and its temperature. Argon-rich $Ar/H_2/CH_4$ gas mixture is used as the precursor during deposition along with an especially designed cooling stage to avoid surface heating in a microwave plasma environment. The deposited diamond films are characterized for structure, microstructure, and residual stresses by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy.

2. Experimental

The diamond films were deposited at low temperatures in a microwave plasma enhanced chemical vapor deposition (MPECVD) system operated at 2.45 GHz. Substrates used were Si (100, p-type) and SiC (6H, n-type) single crystal wafers. For the low temperature diamond growth process, a custom-made stainless steel sample holder compatible with the commercial AX5100 system was designed and fabricated. The sample holder had several features including (i) water cooling, (ii) ability to apply a bias voltage up to 500 V, (iii) height adjustment to form and stabilize the plasma, and (iv) rotation of the sample holder to obtain film uniformity. A graphite disc was placed on top of the stainless steel sample holder stage to form a stable plasma. Regulating the coolant temperature and flow rate controlled the temperature of the sample, which were measured and maintained by a recirculating water bath. The surface temperature of the wafer in the MPECVD environment was measured by an IR pyrometer calibrated to function directly in a microwave plasma environment. To calibrate the pyrometer experimental conditions were simulated except for the vacuum environment and plasma generation. A hot plate was used with a W wafer with Si or SiC sample on top of it similar to the arrangement done during deposition in a CVD chamber. The IR radiation from the heated substrate surface had to transmit through two quartz windows placed at 14 in. above the substrate in the chamber.

The focus of the IR pyrometer was adjusted to fall at the center of the silicon or SiC wafer on the heating stage. Two