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Diamond films with preferred <110> texture by hot filament CVD at low pressure

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ABSTRACT

The effects of gas pressure on the textured growth of diamond films were investigated in a hot filament chemical vapor deposition (HFCVD) system. Diamond thin film with the growth rate of 1.3 μm/h and with high <110> texture was obtained at 5 Torr when lowering the gas pressure from 40 Torr to 1 Torr. The formation of high density nanocrystalline diamond nuclei elongated along the <110> direction in the nucleation stage and its consequent growth at lower pressure were considered to be responsible for the formation of <110> textured diamond thin film.

1. Introduction

Due to their high hardness, high transparency, high thermal conductivity and unique semiconductor characteristics, diamond films synthesized by chemical vapor deposition (CVD) have been extensively studied in the last two decades for their potential applications in mechanics, optics and electronics [1,2]. Among the many CVD methods, hot filament chemical vapor deposition (HFCVD) has been one of the most common methods due to its low capital cost and the ability to scale up. During the HFCVD system, various gas species formed on and near the filament and their transport to substrate play an important role in diamond film growth [3,4]. The transport of active species in a CVD system is affected by numerous parameters, such as the gas pressure, the temperature of filament, the composition of the incoming gas and the extent of chemical reactions on and near the filament. The gas pressure is an important parameter for CVD diamond growth since the gas pressure sensitively changes both the gas phase fluid dynamics and gas phase chemical reaction kinetics among various gas species in a CVD reactor [5,6]. However, the gas pressure used for HFCVD diamond film growth always ranges from several tens to several hundreds Torr, which leads to the diamond nucleation density of 10^7–10^8 cm^{-2} [7–11]. And diamond films with high nucleation density (10^{10}–10^{11} cm^{-2}) have also been obtained by Th. Dikonimos Makris et al. at 30 mbar (22.5 Torr) [12] and by Pecoraro et al. at 15 mbar (11.3 Torr) [13] by applying a negative bias to the substrate. In fact, low pressure is also an effective way to increase the diamond nucleation density. Lee et al. [14] and Jiang et al. [15] reported the high density (10^{10}–10^{11} cm^{-2}) diamond nucleation on mirror polished silicon substrates under very low pressure (0.1 Torr to 1 Torr). And nanocrystalline diamond films with high secondary nucleation rate has also been obtained by Liang et al. under very low pressure (0.125 kPa, 1 Torr) [16]. In fact, not only the diamond nucleation density, but also its textured characteristic will be influenced by the gas pressure due to its influence on the gas phase fluid dynamics and gas phase chemical reaction kinetics [5,6]. However, the evolution of diamond orientation and textured growth of diamond films with high nucleation density at low pressure (several Torr) have not been reported.

In this paper, the influence of pressure on the evolution of diamond orientation and textured growth of thin diamond films has been systematically investigated from a conventional CH_4/H_2 (1%) gas mixture in a HFCVD system. Diamond thin film with the growth rate of 1.3 μm/h and with high <110> texture was obtained at 5 Torr when lowering the gas pressure from 40 Torr to 1 Torr. The surface morphology, orientation, and quality of the deposited diamond films changes dramatically by only varying the growth pressure. The relationship between the diamond film growth rate and the deposition pressure as well as the formation of <110> textured diamond film at low deposition pressure has been discussed.

2. Experimental

The diamond films were deposited in a typical HFCVD apparatus, which is quite similar to that of Chu et al. [17]. The hot-filament was made of a 0.5 mm tungsten wire wound in to 2 mm i.d. and 9 circles. A source gas was fed through a steel nozzle to the substrate after activation with tungsten hot filaments. Mirror polished N-type Si (111) wafer was used as substrates. Prior to deposition, the substrates were ultrasonically cleaned in acetone, de-ionized water and 5% HF to remove the oxide layer, followed by ultrasonic scratching in an acetone suspension with 0.5 μm diamond powder for 60 min. The substrates were then rinsed

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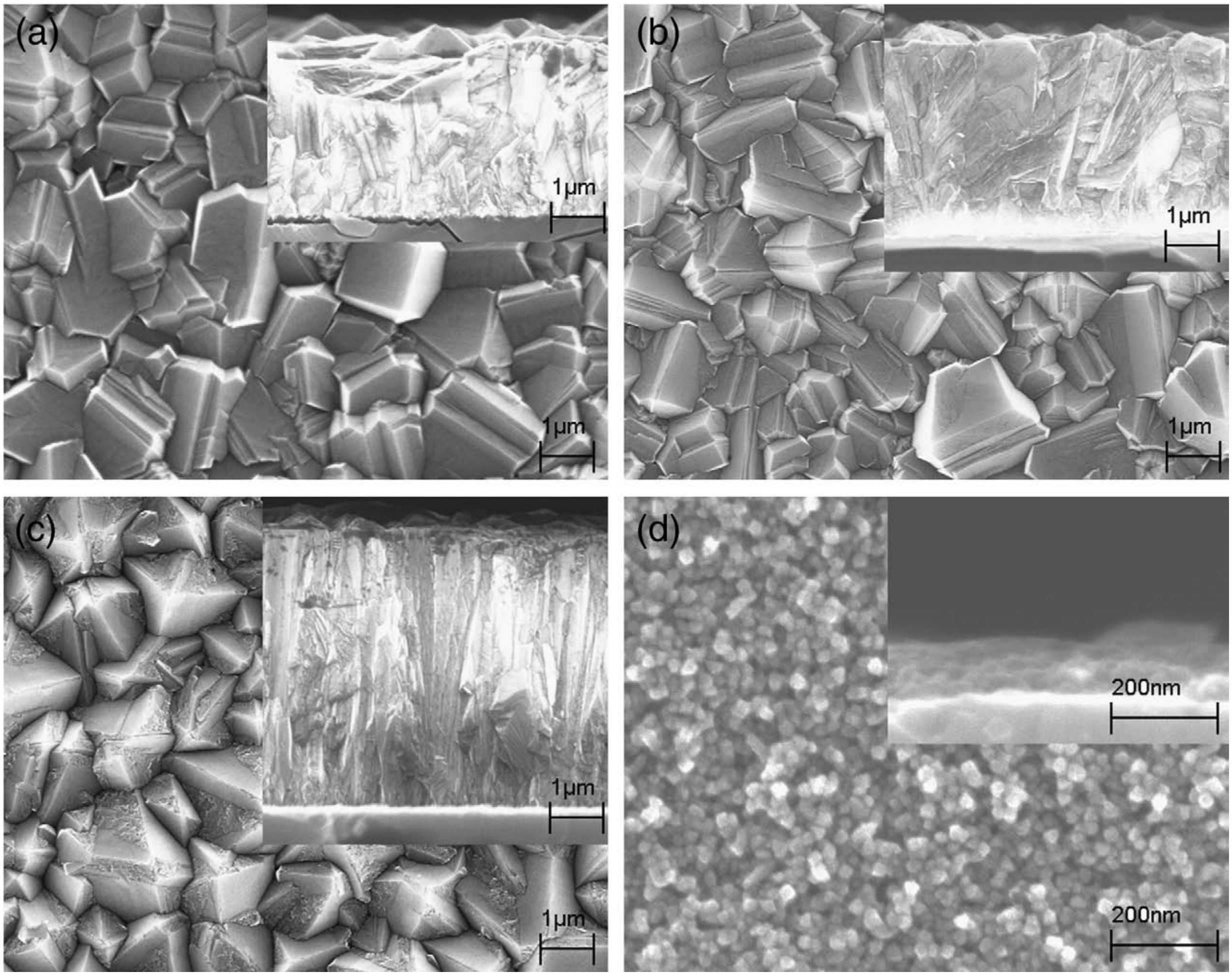

Fig. 1. SEM micrographs of the diamond films deposited for 4 h at different pressure: (a) 40 Torr, (b) 10 Torr, (c) 5 Torr, (d) 1 Torr, the insets are their corresponding cross-section images.

sequentially in de-ionized water, 5% HF and de-ionized water before being loaded into the reaction chamber. The substrate temperature was stabilized at 700 °C by adjusting the distance between the filament (2100 °C) and the substrate to ~7 mm.

The deposition chamber was pre-evacuated down to a vacuum of ~10^{-5} Torr before methane (CH_4) and hydrogen (H_2) were introduced. The working pressure was stabilized at 40 Torr, 10 Torr, 5 Torr, 3 Torr, 2 Torr and 1 Torr, respectively. The diamond deposition was fallen into two stages, nucleation and growth, depending on the composition ratio of CH_4/H_2 gas mixture. The H_2 gas was introduced into the chamber with a constant flow rate of 100 SCCM, while the CH_4 gas was first introduced with a flow rate of 4.0 SCCM to keep the CH_4/H_2 ratio at 4% for 15 min during the nucleation stage, then changed to 1.0 SCCM to keep the CH_4 / H_2 ratio at 1% for 2 h and 4 h respectively during the growth stage.

The deposited films were characterized by scanning electron microcopy (SEM, LEO 1530VP), Micro-Raman spectroscopy (Dilor LabRam-1B) and X-ray diffraction spectroscopy (Cu Kα, $\lambda = 0.1541$ nm, D/max-2200 X-ray Diffractometer) at room temperature. The Raman spectra were obtained using an Ar^+ laser with a wavelength of 514.5 nm. The spot size was approximately 1 μm.

3. Results

Typical SEM micrographs of the films deposited at different pressure for 4 h are shown in Fig. 1, the insets are their corresponding cross-section SEM images. It is shown that randomly-oriented polycrystalline diamond films with well defined crystal shape with thickness of 3.2 μm and 3.8 μm were deposited at 40 Torr and 10 Torr respectively (Fig. 1(a) and (b)). By decreasing the pressure to 5 Torr, most of grains show well-facetted pyramidal shape (Fig. 1(c)). The thickness of this film is 5.3 μm. Only carbon particles with an average grain size of 20 nm and a thickness of 120 nm was deposited by further decreasing the gas pressure to 1 Torr. In order to study the effect of

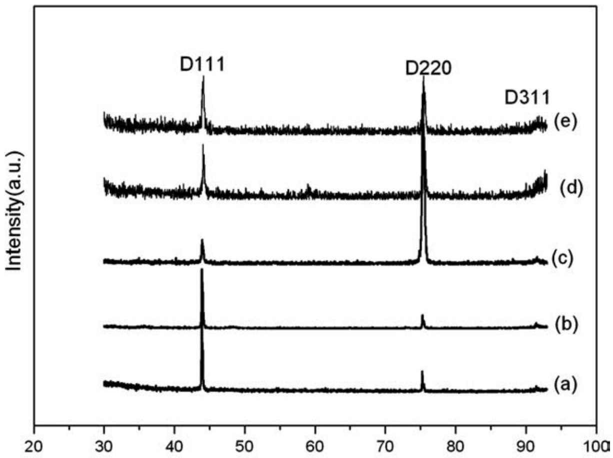

Fig. 2. X-ray diffraction spectra of the diamond films: deposited for 4 h at (a) 40 Torr, (b) 10 Torr, (c) 5 Torr, (d) 3 Torr and (e) 2 Torr.