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Effect of argon and substrate bias on diamond thin film surface morphology

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Abstract

Nanocrystalline materials are of high interest, because mechanical and physical properties of such materials are different from those or coarse-grained type. Continuous and smooth nanocrystalline diamond (NCD) thin films were successfully grown on mirror polished silicon substrates, using double bias plasma-enhanced hot filament chemical vapour deposition technique. A gas mixture of $Ar:CH_4:H_2$ and $CH_4:H_2$ was used as the precursor gas. The effect of the gas composition, flow rate and substrate bias during deposition on diamond crystallite size was investigated. Changing the growth parameters facilitates control of grain size of polycrystalline diamond thin films from microcrystalline to nanocrystalline. The structure of fine-grained NCD films has been studied with scanning electron microscopy and Raman spectroscopy.

Keywords: Nanocrystalline; Diamond film; HFCVD; NCD; Roughness

1. Introduction

The unique properties of diamond, such as extreme hardness, low friction coefficient, chemical inertness, high electrical resistivity, semiconductivity when doped, excellent thermal conductivity and good biocompatibility, make it a very attractive material for a wide spectrum of applications in the field of optical and electronic devices, cutting tools, etc. [1]. In spite of the outstanding physical and mechanical properties of microcrystalline diamond (MCD) film, its relatively high surface roughness has been a significant obstacle in commercial applications, especially for wear-resistant purposes, surface acoustic wave devices and heat sinks for cooling electronic components [2]. In general, the surface roughness of diamond film is known to be closely related to its grain size and surface morphology, which are also affected by the growing conditions. As-grown films of polycrystalline diamond have been reported to reveal surface roughness in the range from hundred nanometres at least to several micrometres [3].

Two solutions can be suggested to overcome the roughness problem, post-polishing which is expensive and time consuming, or naturally grown smooth films with nanocrystalline grain size [4–6]. Nanocrystalline diamond (NCD) thin films can be grown in a variety of ways. The deposition technique used for NCD growth must ensure high re-nucleation rate of secondary nuclei. Most commonly, high re-nucleation rates are obtained by decreasing the relative proportion of hydrogen in methane/hydrogen gas mixture during deposition. This can be also achieved by using noble gas, e.g. argon or even nitrogen. Another method is the application of substrate bias voltage during deposition [7–9]. In this study, NCD films were deposited with hot filament chemical vapour deposition (HFCVD) equipment using both of the mentioned methods.

2. Experimental details

Diamond depositions were carried out in the double bias plasma-enhanced HFCVD reactor described previously [10]. Total pressure in the reactor was 3 kPa. The gases were activated by five 0.8 mm thick and 120 mm long

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tungsten filaments heated to ~2000 °C. The wires were always pre-carburized under 1% of CH_4 in H_2. The substrate temperature was maintained in the range 650–750 °C (measured by a K-type thermocouple mounted on a molybdenum substrate holder) and the distance between the filament and the substrate was 10 mm. For NCD deposition using argon, the deposition process consists of two steps, bias-enhanced nucleation in CH_4:H_2 (3:300 sccm/min) and plasma assisted growth in CH_4:H_2:Ar (3:300:Ar sccm/min) gas mixture, where the Ar flow rate was varied from 0 to 14 sccm/min. The other method using bias-enhanced re-nucleation consists of three steps, bias enhanced nucleation, growth of polycrystalline diamond and re-nucleation (bias enhanced growth), all three were performed in CH_4:H_2 (6:300 sccm/min) gas mixture. Nucleation, the first step used by both methods was carried out at negative substrate biasing −170 V. All steps were supported by positive plasma-biasing of 100 V. Re-nucleation bias was varied from −50 to −150 V. Characterization of diamond coatings was done using scanning electron microscopy (SEM) and μ-Raman spectroscopy (Dilor system working with He–Ne laser of 632.817 nm wavelength).

3. Results and discussion

Fig. 1 shows SEM images of the films deposited under various argon flow rates. The morphology changed from typical microcrystalline diamond (Fig. 1a) with grain size around 500 nm to nanocrystalline (Fig. 1d) with grain size from several nanometres to tenths of nanometres as the argon flow rate increased from 0 to 14 sccm/min. Figs. 1b and c shows diamond crystals disrupted due to decrease in the relative hydrogen proportion in methane/hydrogen/argon gas mixture during deposition. The role of hydrogen in growth of polycrystalline diamond (PCD) films is to etch the non-diamond sp^2 bonds concentrated at the grain boundaries, which serve as predominantly re-nucleation sites for the secondary diamond nuclei. Therefore, in the hydrogen proportion deficient-argon rich gas phase, the re-nucleation rate is higher than at standard polycrystalline diamond growth parameters.

Fig. 2 shows SEM images of the films deposited under various values of applied negative substrate bias. First, typical PCD film (Fig. 2a) was grown using two-step method (bias enhanced nucleation and plasma-assisted growth) and then the MCD film was overgrown by nanocrystalline diamond due to application of the negative substrate bias of −50, −100 and −150 V, respectively (Figs. 2b–d, respectively). Figs. 2b and c shows fine-grained NCD structure on cauliflower-like matrices, caused by the MCD underlayer grain size. Fig. 2d shows NCD film with ballas-type morphology, which is referred to be nearly pure diamond with nanocrystalline structure [11]. Negative bias voltage is generally used for enhancement of the nucleation density in the first step of diamond film deposition. The bombardment of energetic ions creates surface defects, which serves as the nucleation site. If such a negative bias is applied during deposition, the nucleation sites will also be supplied continuously. This will inhibit columnar growth of diamond grain, and thus will reduce the grain size of diamond film [12]. The ion bombardment energy increases with negative bias voltage, which enhances the number of re-nucleation sites during diamond growth. Therefore, the grain size of diamond film will decrease with increasing negative bias voltage.

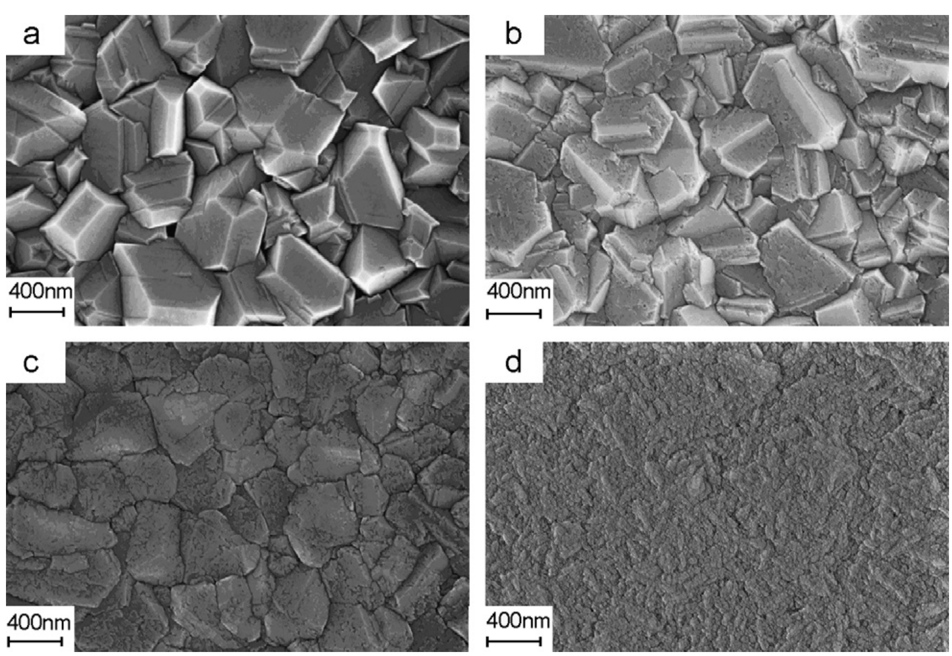

Fig. 1. Surface morphology of the diamond films deposited in $CH_4/H_2/Ar$ gas mixture with increasing argon flow rate: (a) 0 sccm/min; (b) 6 sccm/min; (c) 8 sccm/min; and (d) 14 sccm/min.