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Linear antenna microwave plasma CVD deposition of diamond films over large areas

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A B S T R A C T

Diamond thin films were grown by linear antenna microwave plasma CVD process over large areas (up to 20 × 10 cm^2) from a hydrogen based gas mixture. The influence of the gas composition (H_2, CH_4, CO_2) and total gas pressure (0.1 and 2 mbar) on the film growth is presented. For CH_4/H_2 gas mixtures, the surface crystal size does not show dependence on the methane concentration and total pressure and remains below 50 nm as observed by SEM. Adding CO_2 (up to 10%) significantly improves the growth rate. However, still no significant change of morphology is observed on films grown at 2 mbar. The crucial improvement of the diamond film purity (as detected by Raman spectroscopy) and crystal size is found for deposition at 0.1 mbar. In this case, crystals are as large as 500 nm and the growth rate increases up to 38 nm/h.

1. Introduction

Advanced combination of intrinsic properties like a smooth surface, excellent optical, mechanical and thermal properties, biocompatibility, high affinity for covalent bonding with specific organic molecules, chemical sensitivity, and wet inertness make nanocrystalline diamond (NCD) films a suitable material for various applications [1–4]. For commercialization, large area deposition becomes of high importance. Large area deposition of NCD films is not a trivial technological task due to the requirement for constant growth conditions over a large area. Presently, standard or modified hot filament chemical vapour deposition (HF-CVD) processes are mostly used to deposit diamond films over large areas for commercial applications [5]. The primary advantages of the HF-CVD process are that diamond films can be produced over large areas at moderate growth rate, deposition on complex 3D geometrically-shaped substrates (like cutting tools) and relatively low capital cost. The deposition area can be simply scaled up by increasing the filament length and by adding new filaments. However, there are several drawbacks of HF-CVD systems, such as filament non-stability during the CVD process (i.e. chemical and physical changes with time) resulting in incorporation of impurities from the filament to the grown film and the restriction of using a lower amount of oxygen or methane to minimize filament burning or degradation, respectively.

From the technological point of view, a higher methane concentration is useful for increasing the diamond growth rate but on the other hand, it shifts the poly-crystalline growth into nanocrystal formation with an increased amount of non-diamond phases (sp^2 phases) preferentially located at grain boundaries [6]. Oxygen containing gas species were found to minimize the unwanted non-diamond phases. Especially they are attractive for a low temperature diamond growth [7,8].

A microwave-plasma-assisted CVD process based on surface waves in a linear antenna arrangement has been shown as a promising alternative to the HF-CVD process [9]. This technique resulted in the growth of optically transparent and smooth NCD films over large areas (30 × 30 cm^2). A typical size of diamond crystals was in the range from 5 to 20 nm. The main advantage of such deposition process, except for simple scaling up over large areas, is ability to introduce and use oxygen gas species. However, the influence of gas and process parameters on resulting diamond film properties is still little investigated and understood.

In this work, we present the influence of the gas composition and total gas pressure on the growth of diamond thin films by linear antenna microwave plasma CVD process over large areas (up to 20 × 30 cm^2). We show that both oxygen based chemistry and lower gas pressure enhance the growth rate and diamond purity.

2. Experimental

Diamond thin films were grown on (100) oriented silicon substrates in size up to 4 inch in diameter (On Semiconductors,

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Czech Republic). Before the CVD growth, Si substrates were ultrasonically pretreated in a suspension of deionized water and ultradispersed detonation diamond powder (diameter 5–10 nm, New Metals and Chemicals Corp. Ltd., Kyobashi). Previously we have shown that this procedure yields high seeding densities in the range up to 10^{11} cm^{-2} [10]. Fig. 1 shows a schematic drawing of the used linear antenna microwave plasma enhanced CVD deposition system. The main body of the system is based on the commercially available apparatus used for the solar cell technology (AK 400, Roth and Rau, AG). Some components have been modified to meet process requirements for the diamond CVD growth. The system employs two microwave generators (2.45 GHz, MX4000D, Muegge) working at pulse-frequency up to 500 Hz and maximum power up to 4.4 kW in a pulse at each side of the linear conductor located in the quartz tube. The substrate holder stage can be resistively heated up to 800 °C and moved up/down to control the distance to the antenna. Next, it can be r.f. biased (13.56 MHz, 600 W/500 V) to control energy of ions impinging on the substrate surface.

A series of diamond films were grown from hydrogen-rich gas mixtures of methane (up to 10%) and carbon dioxide (up to 10%). Total gas pressure was 2 or 0.1 mbar. Substrate temperature was kept between 650 and 750 °C.

Surface morphology and grain size of the deposited diamond films were characterized by scanning electron microscopy (SEM, e_LiNE writer, Raith GmbH,). Diamond character of the films was determined from Raman spectroscopy (Renishaw In Via Reflex Raman spectrometer, excitation wavelength of 325 nm). After subtraction of a linear background, the peaks in the Raman spectra were fitted using a linear combination of Gaussian–Lorentzian line shapes (LabSpec V2.08 fi.DILOR).

3. Results

Fig. 2a shows Raman spectra of diamond films deposited at 2 mbar for a varied methane concentration in the range from 0.5 to 10%. All Raman spectra are dominated by D and G bands, i.e. 1360 and 1580 cm^{-1}, respectively [11]. The diamond characteristic peak centred at 1331 cm^{-1} [12] is observed only at low methane concentrations (0.5–1%). Additionally, two weaker broad bands centred at around 1160 and 1480 cm^{-1} are observed. They can be attributed to short transpolyacetylene segments most probably localized at diamond grain boundaries [13]. However, these peaks are still under discussions and some authors attributed them to nanocrystalline diamond films [14,15]. Thickness of all films deposited at 2 mbar from the CH_4/H_2 gas mixture was about 70 ± 15 nm (as determined by a cross section SEM analysis). The calculated deposition rate was very low (5 ± 1 nm/h) within the tested methane range. Surface morphology of the film deposited at 2 mbar and 1% CH_4 is shown in Fig. 2b. The SEM image reveals a flat surface with fine granular structures (5–15 nm). Increasing methane up to 10% resulted in the developing of similar surface morphology while same structures exhibited the tendency in formation of clustered islands (cauliflower like structures, not shown here).

Fig. 2c shows Raman spectra of samples deposited at 0.1 mbar for a varied methane concentration in the range from 1.5 to 10%. Raman spectra are very similar to the spectra of samples deposited at 2 mbar. However, in this case the indication of diamond characteristic line was observed for the methane range 2.5–5%. A small peak is perhaps detectable even up to 10%. In this case the growth rate increased nearly linearly from 9 nm/h (CH_4 = 1.5%) up to 29 nm/h (CH_4 = 10%). The surface morphology slightly changed and larger features in sizes up to 30 nm were observed at 1.5% CH_4 (Fig. 2d). The film thickness was about 130 nm. Some nanocrystals appear arranged in cluster-like features. Increasing the methane concentration up to 10% resulted in the growth of thicker diamond film (up to 430 nm) for the same time period. The surface morphology did not change significantly. Some surface regions exhibited wire-like features consisting of small nanocrystals.

Fig. 3 compares the growth of diamond film at 0.1 and 2 mbar using 2.5% CH_4 in H_2 when 10% of CO_2 was added. Raman spectra in Fig. 3a show dominating D and G bands on sample grown at 2 mbar. Diamond peak at 1330 cm^{-1} is resolvable but at low intensity. Broad bands centred 1160 and 1480 cm^{-1} are observed too. The

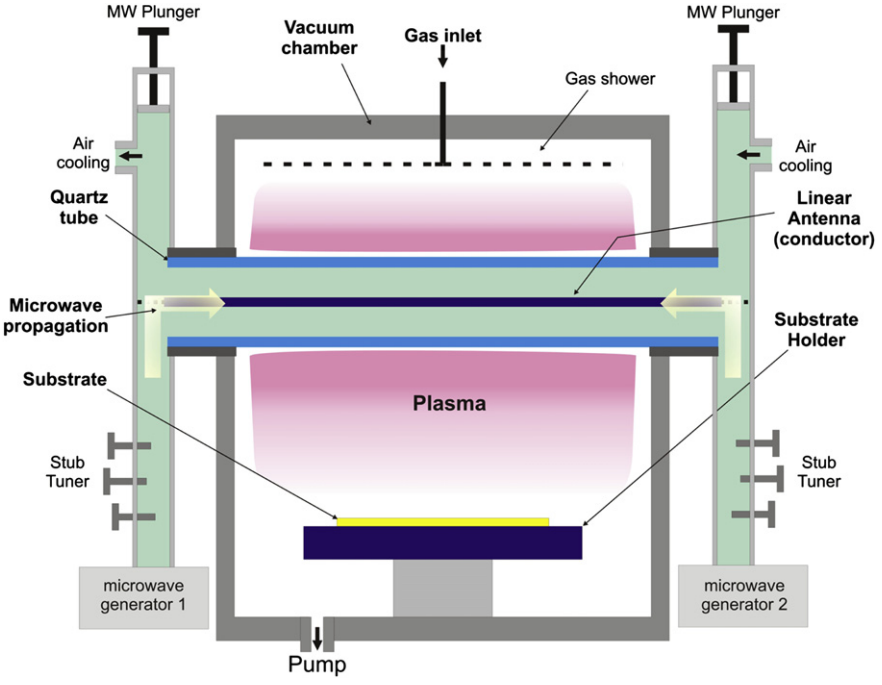

Fig. 1. Schematic drawing of linear antenna microwave plasma enhanced CVD system adapted for diamond deposition.