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978-1-605-11259-6 - Materials Research Society Symposium Proceedings Volume 1282:

Diamond Electronics and Bioelectronics—Fundamentals to Applications IV

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Excerpt

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Diamond Growth

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Mater. Res. Soc. Symp. Proc. Vol. 1282 © 2011 Materials Research Society

DOI: 10.1557/opl.2011.524

Routes towards large area, low pressure nanodiamond growth via pulsed microwave linear antenna plasma chemistryMichael Liehr¹, František Fendrych², Andrew Taylor², Miloš Nesládek³¹Leybold Optics Dresden GmbH, Dresden, Germany²Institute of Physics, Academy of Sciences of the Czech Republic, v.v.i. Prague 8, Czech Republic³IMOMEC division, IMEC, Institute for Materials Research, University Hasselt, Wetenschapspark 1, B3590 Diepenbeek, Belgium**ABSTRACT**

Current experimental configurations for MW PECVD diamond growth do not allow simple up-scaling towards large areas, which is essential for microelectronic industries and other applications. Another important issue is the reduction of the substrate temperature during diamond growth to enhance the compatibility with wafer processing technologies. Such advantages are provided by MW-linear antenna (LA) plasma applicators, allowing a scalable concept for diamond growing plasmas. In the present work we introduce a novel construction of LA MW applicators designed for nanodiamond growth by using plasmas ranging from continuous wave (CW) to high repetition rates pulsed modes (up to 20 kHz) which advantages are discussed in detail.

INTRODUCTION

Due to its excellent properties diamond layers in the form of nanocrystalline has been identified as having potential industrial uses from MEMs devices to biomedical devices and to protective coatings. The growth of such layers has been described in [1, 2 and 3]. Typically the conditions for growth are a mix of H₂ and CH₄ using microwave plasma enhanced (MW PECVD). To maximise the industrial potential of NCD layers it is necessary to grow on large areas and at temperatures compatible with the substrate.

Microwave plasma enhanced discharges used for the growth of diamond need to operate at high pressures (few mbar up to several hundred mbar) since growth rates are low [4]. Ball or hemisphere type plasma discharges of several cm diameter fed by several kW of power are extremely destructive. Therefore atmosphere-to-vacuum interfaces need to stay clear of such plasma discharges. However, this is not easy to achieve since the power density is usually highest at the inner surface of the interface and that is where the plasma will ignite preferably. Microwaves can be used to overcome this by using transversal magnetic (E) modes of propagating microwaves in cylindrical waveguides which have a concentration of electric field around the axis of symmetry of the cylinder (the plasma discharge vessel) and to ensure the atmosphere to vacuum interface is not located near this region of the cylinder. The plasma would then ignite and remain at the area of highest electric field. TM₀₁ (or E₀₁) is the preferred mode of operation and is easy to create by terminating a coaxial line by letting the inner conductor end and the wave will propagate without the inner conductor. Typical MW PECVD systems using the above method, with reasonable growth rates, are restricted to an area of diameter of 15cm and with growth temperatures above 600°C and therefore is unattractive for industrial scale production of NCD

In the described work we use coaxial plasma lines which are similar in the way that the outer conductor of a coaxial line is replaced by a plasma which is located very near to the outer surface of the tube shaped atmosphere to vacuum interface. To bring this much power into the discharge, the interface area must be large to reduce etching and heat load. These conditions are ideal for large area low pressure processes and applications as described in [5, 6 & 7]. Linear antenna (LA) plasma applicators used here allow a scalable concept for diamond growing plasmas. In the present work we introduce a novel construction of LA MW applicators designed for nanodiamond growth by using plasmas ranging from continuous wave (CW) to high repetition rates pulsed modes (up to 20 kHz) which advantages are discussed in detail.

Using fast pulsing provides important advantages for diamond growth. Firstly, it allows the application of high power in short pulses, due to non-linear MW absorption and consequently a reduction of total average input power to ~ 4W/cm² compared to ~ 20 W/cm² for CW LA-MWs or to typically 100-200W/cm² for resonance cavity applicators. Despite the factor of 50 power reduction, the diamond growth rate that can be obtained at 450°C is comparable to or higher than that of resonance cavity systems.

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Our system by using high frequency pulsed microwaves enhances the plasma concentration (i.e. where MW absorption increases non-linearly with the power due to non-linear electron acceleration in strong microwave fields), leading to an increase in the concentration of atomic hydrogen and therefore opens new ways to maximize growth rates at low temperatures.

Secondly, the pulsed plasma concept brings significant improvements in diamond quality when compared to the CW mode. The resulting diamond films, grown by pulsed plasma, show clean grain boundaries with columnar growth, i.e. resembling classical nano-crystalline diamond (NCD) films of high crystallinity. This is achieved by the use of tailored plasma chemistry. In fact the concentration of atomic hydrogen can be sustained with sufficiently high values during the power-off periods at the right pulse frequency, while the growth rates in the off-period is significantly reduced. This allows suppression of re-nucleation during the growth and preparation of high quality NCD films with 2-5% sp^2 carbon (based on Raman measurements), for layer thicknesses ranging from 30 to 300 nm.

EXPERIMENT

For the growth of NCD films a Microwave Plasma Enhanced Linear Chemical Vapour Deposition (MWPELCVD) apparatus was built. The MWPELCVD apparatus is capable of producing microwave (2.45GHz) pulses to a maximum of 2 x 10kW from conventional 3 kW c/w magnetron tubes, with pulse widths (peak to peak) from 110ms - 40 μ s (9Hz - 25kHz, note: restricted to 15kHz at full MW power) at duty cycles of 30%. The growth chamber allows the deposition on substrates up to the size of 300mm x 500mm. Microwaves are delivered into the growth chamber by four pairs of coaxial antennas enclosed in quartz envelopes and powered from both ends. The linear microwave plasma sources are arranged parallel to one another above the substrate holder (see Fig. 1).

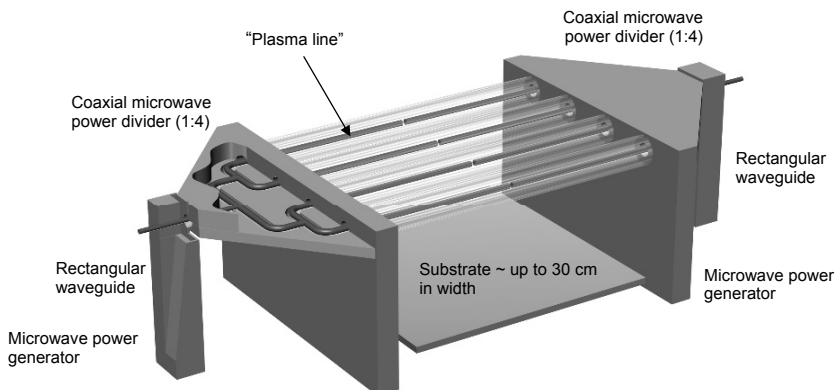


Fig. 1: Plasma line concept for large area coating

Several NCD films have been produced using the following typical process conditions: Gas mixtures – H_2 , CH_4 and CO_2 with various ratios, process pressure range – 0.5 mbar to 2mbar, microwave power – up to 10.0 kW pulsed and growth time of up to 8 hours. Substrates are mounted on a molybdenum holder. During growth, substrate holder temperatures were measured to be in the region of 450°C. Typical substrates used are silicon, quartz and stainless steel. Substrates were seeded with a nanodiamond dispersion (NanoAmando[®]B) from NanoCarbon Research Institute Ltd. Prior to seeding this dispersion was sonicated to break up any large clusters. Dynamic light scattering (DLS) showed that after sonication the average mean size of the dispersion was 4 – 6nm. Following sonication clean substrates were dipped into the dispersion and then spin coated to produce a mono layer of seeds and also to further remove unwanted large particles. This process resulted in homogenous coverage

of substrates with a nucleation density of approximately 10^{10}cm^2 as measured using atomic force microscopy (for Si substrates) which is comparable to [7].

CH₄	5%
H₂	92%
CO₂	3%
Chamber pressure	1.5 mbar
Microwave power	8kW Peak (2.5kW average)
Substrate temperature	600°C – 450°C
Pulse frequency range	2.3kHz, 34.5kHz and 14.3kHz

Table 1: Table showing range of typical growth conditions used in depositions

Grown films were investigated with the following techniques: Atomic Force Microscopy (AFM) measurements were performed with a NTEGRA Prima NT MDT system under ambient conditions. Samples were scanned using a HA_NC Etalon tip using semi contact mode. Secondary Electron Microscopy (SEM) images were produced of grown films using a FEI Quanta 3D FEG which combines high resolution scanning electron microscope with focused ion beam (DualBeam). Raman spectroscopy was carried out at room temperature using a Renishaw InVia Raman Microscope with the following conditions: Wavelength = 488 nm (25 mW), x50 Olympus objective, 65 μm slits, spot focus, Grating = 2400 l/mm.

RESULTS AND DISCUSSION

AFM and SEM were all used to measure the growth rates and quality of layers grown using different conditions. Measured growth rates using the two techniques were found to be in good agreement (see Fig. 2). The growth rate trends seen in Fig. 2 show that with the increase in pulse frequency, growth rates increase. This increase can be attributed to the presence of higher concentrations of atomic H due to reduction in the H recombination rate at higher frequencies, or more specifically when the pulse of time is reduced. This increase in H with pulse frequency has been demonstrated by optical emission spectroscopy as reported in [7]. The effect of growth rate increase due to enhanced atomic H concentration is well known and has been investigated in previous works [9].

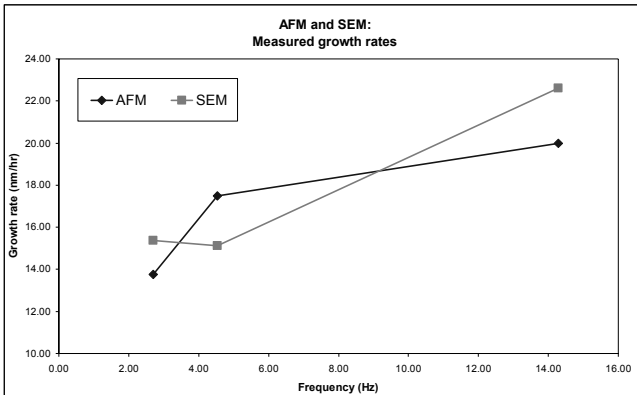


Fig. 2: Effect of increase in pulse frequency on NCD growth rate measured by AFM and SEM.

AFM and SEM confirmed that the layers grown were continuous and without holes. SEM further confirmed that the layers were columnar in nature and of good crystalline structure (see Fig. 3).

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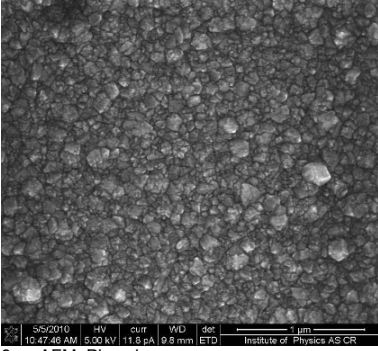
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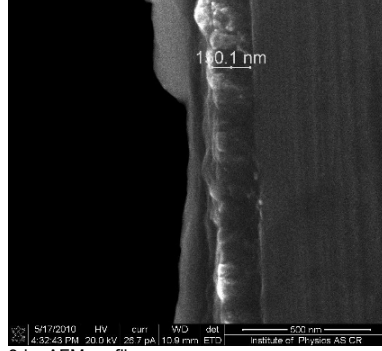
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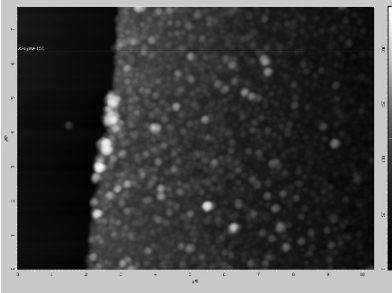
3a – SEM: Plan view



3b – SEM: Cross section view



3c – AFM: Plan view



3d – AFM profile

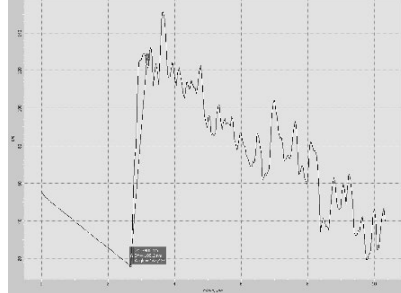


Fig. 3: SEM and AFM images of NCD layer grown using high frequency (14.3kHz) showing complete coverage and columnar like structure. (AFM image area = $10\mu\text{m} \times 10\mu\text{m}$)

Raman spectroscopy (see fig. 4) showed peaks relating to diamond growth (sp^3) and amorphous carbon (sp^2) in layers investigated. It was found that an increase in the pulse frequency significantly reduced the level of sp^2 in the grown layers. Using the method described in [10], the percentage of sp^3 was calculated to increase from 85% to 95% with increasing pulse frequency. This trend matches that of the growth rate data previously described and can be explained similarly, i.e. at higher H concentrations sp^2 is preferentially etched.

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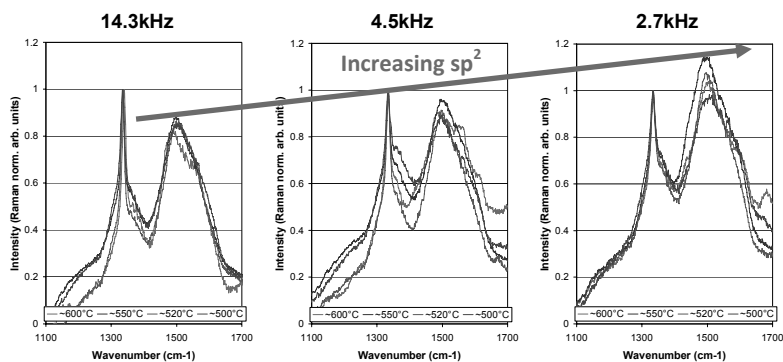
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Fig. 4: Effect of increase in pulse frequency on sp^2 content of NCD layers. See **Table 1** for growth parameters.

CONCLUSIONS

Using the combination of coaxial plasma lines and high frequency pulsed microwaves the growth of high quality nano-crystalline diamond over large areas and at low temperatures has been demonstrated. Growth rates and material quality (sp^2 content) have been further improved by “tuning” the frequency of the microwave pulses to increase the levels of atomic H.

ACKNOWLEDGMENTS

Thanks to Masataka Hasegawa (AIST, Japan), Mike Ashfold (Bristol Uni. UK) Yuri Mankelevich (Moscow) for fruitful discussions. Financial support from the Academy of Sciences of the Czech Republic (grants KAN200100801, KAN300100801, KAN301370701 & KAN400480701), the MSMT CR grant COST-LD11076, the European R&D projects (FP7 ITN Grant No. 238201 - MATCON and COST MP0901 - NanoTP) and specific university research (MSMT no. 21/2010) are gratefully acknowledged.

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Mater. Res. Soc. Symp. Proc. Vol. 1282 © 2011 Materials Research Society

DOI: 10.1557/opl.2011.438

Simulations of CVD Diamond Film Growth: 2D Models for the identities and concentrations of gas-phase species adsorbing on the surfacePaul W. May¹ and Yuri A. Mankelevich²¹School of Chemistry, University of Bristol, Bristol, BS8 1TS, United Kingdom.²Skobel'tsyn Institute of Nuclear Physics, Moscow State University, Leninskie gory, Moscow 119991, Russia.**ABSTRACT**

A prerequisite for modelling the growth of diamond by CVD is knowledge of the identities and concentrations of the gas-phase species which impact upon the growing diamond surface. Two methods have been devised for the estimation of this information, and have been used to determine adsorption rates for C_xH_y hydrocarbons for process conditions that experimentally produce single-crystal diamond, microcrystalline diamond films, nanocrystalline diamond films and ultrananocrystalline diamond films. Both methods rely on adapting a previously developed model for the gas-phase chemistry occurring in a hot filament or microwave plasma reactor. Using these methods, the concentrations of most of the C_xH_y radical species, with the exception of CH₃, at the surface have been found to be several orders of magnitude smaller than previously believed. In most cases these low concentrations suggest that reactions such as direct insertion of C₁H_y (y = 0-2) and/or C₂ into surface C-H or C-C bonds can be neglected and that such species do not contribute significantly to the diamond growth process in the reactors under study.

INTRODUCTION

Chemical vapor deposition (CVD) of diamond is a maturing technology that is beginning to find many commercial applications in electronics, cutting tools, medical coatings and optics [1]. The CVD process usually involves the gas-phase activation of a gas mixture containing a small quantity of a hydrocarbon in excess hydrogen [2]. A typical gas mixture uses a few %CH₄ in H₂ (plus sometimes additional Ar or N₂), and depending upon the growth conditions this produces polycrystalline films with grain sizes from ~5 nm to mm. Films with grain sizes less than 10-20 nm are often called ultrananocrystalline diamond (UNCD) films; those with grain sizes a few 10s or 100s of nm are nanocrystalline diamond (NCD); those with grain sizes microns or tens of microns are termed microcrystalline diamond (MCD); and those with grain sizes approaching or exceeding 1 mm are single-crystal diamond (SCD).

In a hot filament (HF) or microwave (MW) plasma CVD reactor, the substrate is exposed to large number of hydrocarbon species, as well as to atomic H and C, and the interplay between various gas-surface processes, such as adsorption of hydrocarbon radicals (mainly CH₃), etching, surface migration, and bonding to the diamond structure, controls the morphology and growth rate of the resulting diamond film. Using these ideas, and following a similar procedure to that of Netto and Frenklach [3], we developed a simplified one-dimensional kinetic Monte Carlo (KMC) model of the growth of diamond films [4], initially for a fixed set of process conditions and substrate temperature. Although the model was only 1D, the interplay between adsorption,

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etching/desorption and addition to the lattice was qualitatively modelled using known or estimated values for the rates of each process. More recently we extended the KMC model of SCD growth to include the temperature dependence of the various surface processes [5]. Our most recent KMC paper [6] involves simulating diamond growth using as input data the experimental reactor conditions used to deposit SCD, MCD, NCD and UNCD. The first consideration was that for some conditions (e.g. those used for UNCD deposition) the concentrations of other C_1 species, in particular C atoms, may no longer be negligible in comparison to that of CH_3 . Thus, we needed to determine the rates of adsorption for *all* relevant hydrocarbon radical species onto the surface, and decide their subsequent fates. Some of this information can be determined spectroscopically [7], however, we now describe how the data from previously published [8] simulations of the gas-phase chemistry can be re-evaluated in order to estimate the concentrations for all the important C_1 species at the diamond surface.

THEORY

In order to study a range of deposition conditions used for growth of different types of diamond we require knowledge of the concentrations of atomic H, CH_3 and the remainder of the other C_1 hydrocarbon radicals (C, CH, CH_2) at the growing diamond surface, all as a function of deposition conditions (pressure, T_s , etc.). These parameters have been calculated using the finite-difference model described in Ref.[8] for the gas mixtures and conditions used experimentally to deposit SCD, MCD, NCD and UNCD in both hot filament (HF) and microwave (MW) reactors. Briefly, MCD conditions are 1% CH_4/H_2 at 20 Torr in a HFCVD reactor with substrate temperature $T_s \sim 1173$ K; NCD conditions are the same except using 5% CH_4/H_2 ; UNCD(HF) conditions used the same reactor but with 80%Ar/18.5% $H_2/1.5\%CH_4$ at 100 Torr; UNCD(MW) films were deposited using 1% $CH_4/1\%H_2/98\%Ar$ in a 700 W MW plasma at 170 W and a reduced $T_s \sim 873$ K; and SCD conditions are for a high density, 600 W MW plasma at 180 Torr using 10% CH_4/H_2 and $T_s \sim 973$ K.

The model uses a database of known chemical reactions along with their temperature-dependent rates to calculate a steady-state gas composition throughout the plasma ball or filament-to-substrate region. The model calculates the concentrations of species as a function of position, z , above the diamond surface, but is restricted in resolution to the grid size, dz , the value of which was chosen to be 0.5 mm based upon the limitations of computation speed. Figures 1(a) and 1(b) show an example of such data for SCD conditions for a sub-set of the species present. The data in Fig.1 taken from Ref. [8] for species concentrations *near* the substrate equate to a distance of $z = 0.5$ mm in the model. Previously we have assumed that the species concentrations at the surface ($z = 0$) can be taken to be the same as those calculated at $z = 0.5$ mm. However, near the surface there is often a thin boundary layer (<1 mm) in which temperatures, gas flows and concentrations can change significantly. Previously, the only species considered to have any significant effect upon diamond growth were H and CH_3 , which (as can be seen in Fig.1(b)) have relatively weak dependences of concentration with z for $z < 5$ mm, despite the steep temperature drop over this distance. As a result, our previous assumption that the concentration of CH_3 at $z = 0$ can be taken to be the same as that at $z = 0.5$ mm is reasonable. However, such an assumption would be incorrect for the other hydrocarbon species, whose dependences of concentration with z near the surface are much stronger. We have tackled this problem using two approaches: