Diamond & Related Materials 47 (2014) 27–34

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Large area deposition of boron doped nano-crystalline diamond films at low temperatures using microwave plasma enhanced chemical vapour deposition with linear antenna delivery

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ARTICLE INFO

Article history:
Received 25 March 2014
Received in revised form 5 May 2014
Accepted 7 May 2014
Available online 14 May 2014

Keywords:
Large area
Low temperature
Boron doped Nano-Crystalline Diamond
Linear antenna MW PE CVD

ABSTRACT

We report on the preparation and characterisation of boron (B) doped nano-crystalline diamond (B-NCD) layers grown over large areas (up to 50 cm × 30 cm) and at low substrate temperatures (<650 °C) using microwave plasma enhanced linear antenna chemical vapour deposition apparatus (MW-LA-PECVD). B-NCD layers were grown in $H_2/CH_4/CO_2$ and H_2/CH_4 gas mixtures with added trimethylboron (TMB). Layers with thicknesses of 150 nm to 1 μm have been prepared with B/C ratios up to 15000 ppm over a range of CO_2/CH_4 ratios to study the effect of oxygen (O) on the incorporation rate of B into the solid phase and the effect on the quality of the B-NCD with respect to sp^3/sp^2 ratio. Experimental results show the reduction of boron acceptor concentration with increasing CO_2 concentration. Higher sp^3/sp^2 ratios were measured by Raman spectroscopy with increasing TMB concentration in the gas phase without CO_2. Incorporation of high concentrations of B (up to 1.75×10^{21} cm^3) in the solid is demonstrated as measured by neutron depth profiling, Hall effect and spectroscopic ellipsometry.

1. Introduction

Due to their excellent properties, diamond layers in the form of nano-crystalline (NCD) have 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 [1–3]. To further enhance the electronic properties of NCD layers it is possible to dope with boron (B) to produce p-type doping and therefore enable diamonds' unique semiconductor properties, such as wide bandgap and high conductivity which, for example, are key for electrochemistry applications.

Typically, B-NCD layers are grown from a mix of H_2 and CH_4 plus the addition of B in the form of, among others, trimethylboron (TMB), diborane or $B(OCH_3)_3$ using microwave plasma enhanced (MW PECVD) [4,5] or hot filament (HF CVD) [6,7] chemical vapour deposition techniques with a substrate temperature of 600–1000 °C. To maximise the industrial potential of B-NCD layers it is necessary to grow over large areas and at temperatures compatible with substrates. Typical cavity based MW PECVD systems are restricted to an area of diameter of 15 cm and with growth temperatures above 600 °C. HF CVD systems do allow for the deposition of B-NCD on large areas but at temperatures above 600 °C. As reported in [3] for MW PECVD and in [6] for HF CVD, depending on conditions used, growth rates can vary from 100 nm/h up to above 10 μm/h. Recently, the growth of B-NCD layers on top of intrinsic layers at temperatures below 600 °C using MW PECVD [8] and B-NCD layers grown using HF CVD systems with high CH_4/H_2 ratios (>5%) [9] have been reported demonstrating the interest in low temperature B-NCD deposition. The use of microwave plasma enhanced linear antenna chemical vapour deposition apparatus (MW-LA-PECVD) has been recently developed [10–12] for the growth of NCD layers. In this method a surface wave is sustained linearly along antennas, therefore the size of microwave discharge is not limited by the wavelength of inputted microwave power. Owing to the diffuse plasma properties, due to a combination of, low process pressure, low electron temperature (1.5 eV), with a high plasma density ($>10^{11}/cm^3$) [12] enabling high atomic hydrogen concentrations even at low power densities [13], the MW-LA-PECVD system enables growth with good homogeneity over large areas at low temperatures (<600 °C). In addition to this, the MW-LA-PECVD system is of a modular design (in all axes) and therefore scalable making it more attractive than cavity based MW or HF CVD systems for industrial (wafer scale production) application. These linear antenna systems typically require the addition of oxygen containing gas (typically carbon dioxide) to enhance growth rates and NCD quality.

As oxygen containing gases lead in general to the reduction of the active B incorporation, in this work we have investigated the influence of

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http://dx.doi.org/10.1016/j.diamond.2014.05.002
0925-9635/

the growth chemistry (CO_2 and TMB content) for the growth of B-NCD layers using MW-LA-PECVD apparatus. The structural, optical and electronic properties have been investigated using a variety of techniques in order to find optimum conditions for B-NCD growth in large-area low pressure non resonant MW PECVD systems.

2. Experiment

B-NCD films were grown on quartz, glass and Si substrates (1 cm^2) in a MW-LA-PECVD apparatus. This apparatus currently can deposit over areas of up to 50 cm × 30 cm and has been described in [11]. B-NCD films were prepared using similar conditions as described in [10], with a $H_2/CH_4/CO_2$ gas mixture at process pressures of <1 mbar and MW powers of 3 kW, with the addition of TMB with and without CO_2. B/C ratios were set up to 15000 ppm and ratios of CO_2/CH_4 between 0 and 0.6. Substrate temperature (650 °C to 600 °C) was monitored during growth using a Williamson Pro 92-38 infrared pyrometer.

Substrates were seeded with a nanodiamond dispersion (NanoAmando®B) from NanoCarbon Research Institute Ltd with an average mean crystal size of 4–6 nm as measured by dynamic light scattering (DLS) after sonication. Following sonication clean substrates were dipped into the dispersion and then spin dried to remove unwanted large particles. This process resulted in a homogeneous coverage of substrates with a nucleation density of approximately 10^{10} cm^{-2} as measured using Atomic Force Microscopy on Si substrates. This result is comparable to [14].

Properties of B-NCD layers were investigated using several characterisation techniques.

Surface roughness and morphology were investigated by Atomic Force Microscopy (AFM) using a NTEGRA Prima NT MDT system under ambient conditions. Samples were scanned using a HA_NC Etalon tip using semi contact mode. To check the homogeneity of the samples the roughness was measured at least at two different positions on the sample. Moreover, at all positions two pictures with areas of 3 × 3 um^2 and 5 × 5 um^2 were measured with 256 × 256 points per picture. The differences in the RMS roughness between different positions at the sample and different scan areas were found to be small, not exceeding 15%, which indicates good homogeneity of the samples. To better visualize surface morphology measure by AFM, local contrast (LC) filtering was used.

Scanning Electron Microscopy (SEM) images were acquired at low accelerating voltages 2–5 kV using a FEI Quanta 3D FEG. Layer thickness was evaluated from an intentionally broken edge producing a clean cross section.

Raman spectroscopy was carried out at room temperature using a Renishaw inVia Raman microscope with the following conditions: Wavelength = 488 nm, nominal output power = 25 mW, with laser power at sample 6 mW, ×50 Olympus objective, 65 μm slits, spot focus, and grating = 2400 l/mm. A high pressure high temperature Ib single crystal diamond was used as a reference for the sp^3 Raman peak position.

Ellipsometry measurements, which have been shown to be sensitive and effective for B-NCD non-destructive optical and structural characterisation [15–17] were carried out using a VASE ellipsometer (Woollam) with a wavelength range of 190 nm–2400 nm. Spectra were recorded in reflection for three angles of incidence (60, 65, and 70°) and were analysed simultaneously with nearly normal reflectivity and transmission measured with the same instrument. The structure of B-NCD films is approximated by a single layer on the quartz semi-infinitive substrate for spectra analysis. Surface roughness was also accounted for by an overlayer containing 50% of voids and 50% of B-NCD (Bruggeman effective medium approximation) [18]. Optical constants of quartz were obtained from uncoated substrate measurements. Spectral dependence of B-NCD electric permittivity was parameterized by the sum of Drude and Tauc–Lorentz terms. The Drude term

$$\varepsilon_{Drude} = \varepsilon_\infty - \frac{A}{E^2 + iBE}$$

which is dominant in IR spectral range generally describes intra-band electronic transitions. In the case of B-NCD films it mainly consists of the absorption of light by free holes in the valence band. From two of the Drude parameters amplitude *A* and broadening *B*, free hole concentration and their mobility can be determined. A free hole effective mass of $0.3m_e$ was used for this calculation [19]. Plasmon frequency ω_p of collective charge excitation is related to parameter *A* by relation [20].

$$A = \varepsilon_\infty \left(\hbar\omega_p\right)^2.$$

Inter-band electronic transitions between σ bands (sp^3 hybridized C), π bands (sp^2 hybridized C in NCD grain boundaries) or between σ and π bands take place in VIS and UV spectral range [21] and are approximated in the spectral range measured by single Tauc–Lorentz term ε_{TL}. Its imaginary part takes the following form

$$\begin{array}{ll} \varepsilon_{TL,2} = \dfrac{AE_0C\left(E-E_g\right)^2}{\left(E^2-E_0^2\right)^2 + CE^2}\cdot\dfrac{1}{E} & E>E_g \\ \varepsilon_{TL,2} = 0 & E<E_g \end{array}.$$

The real part $\varepsilon_{TL,1}$ is calculated by Kramers–Krönig relations. Diamond quality can be estimated by comparison of Tauc–Lorentz function with optical constants of single crystalline diamond, not containing any defect site of sp^2 hybridized C, and hence fully transparent up to 5.4 eV (onset of the first indirect electronic transition).

Titanium (20 nm)/gold (100 nm) triangle contacts were evaporated in the corners of square (~10 × 10 mm^2) samples for electrical characterisation of B-NCD films. The ohmic character of the contacts was always checked. Conductivity and Hall constant were measured by differential van der Pauw method using a Keithley 6221 current source and two electrometers, Keithley 6514 with nanovoltmeter and Keithley 2182A which recorded voltage difference between the electrometers. Pulsed (quasi-DC) measuring mode was used to compensate for parasitic thermoelectric signals. All electrical measurements were performed in dark and at room temperature (296 K ± 1 K). In all films investigated the resistivity has been measured within errors not exceeding 1–2% and the Hall constant and mobility have been established with an accuracy of about 5%.

The resistivity values were stable over a time scale of days. Because the hydrogen termination related conductance usually exhibits significant time dependence reflecting ambient variations [22,23] we can assume that this transport channel does not play a substantial role in our samples.

Samples were analysed by neutron depth profiling (NDP) [24,25] which is a well-established, non-destructive technique for determining depth profiles of selected light elements (e.g., ^3He, ^{10}B, and ^6Li). This technique has been shown to give atomic boron concentrations consistent with SIMS analysis results [26]. NDP is based on specific nuclear reactions induced by thermal or subthermal neutrons which are accompanied by emission of charged particles as reaction products. Samples were irradiated with thermal neutrons from a 6 m long neutron guide, installed at the LWR-15 research nuclear reactor (Research Centrum Rez, Czech Republic). Typical thermal neutron flux at the sample position was 10^7 cm^{-2} s^{-1} (with a cadmium ratio >$10e^5$). The reaction products, alpha particles and lithium ions from the nuclear reaction $^{10}B(n_{th}, \alpha)$ ^7Li, were registered by a semiconductor detector (Hamamatsu PIN diode, with a 10 × 10 mm^2 sensitive area), placed at a distance of several cm from the sample (with a detector solid angle $\omega = 10^{-3}$). The energy of the particles was analysed by a MPA-3 multichannel spectrometric system with an energy resolution (FWHM) of about 15 keV. The energy spectra of the reaction products were evaluated off-line by a lab-made PC program, where the boron depth profile was determined on a channel-by-channel basis. This procedure is acceptable due to the sufficiently low concentration of boron in the samples. The alpha particle