



Synthesis and characterization of boron incorporated diamond-like carbon thin films

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ABSTRACT

Boron incorporated diamond-like carbon (B-DLC) (up to 8 wt.% boron) thin films were synthesized on silicon wafers using biased target ion beam deposition technique, where diamond-like carbon (DLC) was deposited by ion beam deposition and boron (B) was simultaneously incorporated by biased target sputtering of a boron carbide (B_4C) target under different conditions. Pure DLC films and B-C films were also synthesized by ion beam deposition and biased target sputtering of B_4C under similar conditions, respectively, as reference samples. The microstructure and mechanical properties of the synthesized films have been characterized by various technologies. It has been found that B exists in different states in B-DLC, including carbon-rich and B-rich boron carbides, boron suboxide and boron oxide, and the oxidation of B probably occurs during the film deposition. The incorporation of B into DLC leads to the increase of sp^3 bonded carbon in the films, the increase of both film hardness and elastic modulus, and the decrease of both surface roughness and friction coefficient. Furthermore, the content of sp^3 bonded carbon, film hardness and elastic modulus increase, and the film surface roughness and friction coefficient decrease with the increase of B-rich carbide in the B-DLC films.

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1. Introduction

Diamond-like carbon (DLC) thin films have been attracting significant interest from both academic and industrial communities due to their unique properties, such as high hardness, high wear and corrosion resistance, low friction coefficient, high chemical inertness, optical transparency and good biocompatibility [1]. Especially, due to their amorphous nature, their properties, including thermal stability, hardness, internal stress, tribological property, electrical conductivity, surface energy, biocompatibility, and adhesion, can be finely tailored to desired values for specific applications by incorporation of different elements in their structures [2]. Those elements include metals, e.g. titanium (Ti), tungsten (W), cobalt (Co), and nickel (Ni) [3–6], nonmetals, e.g. boron (B), silicon (Si), nitrogen (N), and fluorine (F), and their combinations [7].

B incorporation to DLC has been receiving increasing research interest because B incorporated DLC (B-DLC) thin films have been found to exhibit increased thermal stability [8], improved electron field emission [9], increased hardness and reduced film stress [10] with great potential for electronic and mechanical applications. The techniques currently used to synthesize B-DLC films include magnetron sputtering, mass-separated ion beam deposition, plasma-enhanced chemical vapor deposition (CVD), and pulsed laser deposition. However, those techniques suffer from their limitations and it's difficult to use them to prepare high quality

B-DLC films to meet the demands of many applications. Therefore, there is a need to develop new processes that could synthesize B-DLC films with higher quality. In addition, the structure of B-DLC and its effects on the film properties have not been fully investigated and understood.

Recently, a biased target ion beam deposition (BTIBD) technique has been developed to overcome some drawbacks of conventional sputtering methods. Comparing to the conventional methods, it can operate at lower pressure (one order of magnitude lower than that in magnetron sputtering) and low temperature (without any extra heating, close to room temperature), and has much less film contaminations due to the use of gridless end-Hall (EH) ion source instead of the gridded ion sources in regular ion beam deposition systems and the use of biased target ion beam sputtering instead of magnetron sputtering [6]. This technique has been used to produce smooth, uniform, and high quality DLC based films including pure and N incorporated DLC [11], Co incorporated DLC [6], Ti incorporated DLC [3], W incorporated DLC [5], and Ni incorporated DLC [4]. However, no work has been reported on the synthesis of B-DLC films by BTIBD and their characteristics. In this work, we report the first results on the synthesis of B-DLC thin films with different B concentrations using the newly developed BTIBD technique and the characterization of structure and properties of the synthesized films.

2. Experimental details

The thin film samples were prepared using the BTIBD system which was custom designed and manufactured by 4Wave Inc. It consists of a

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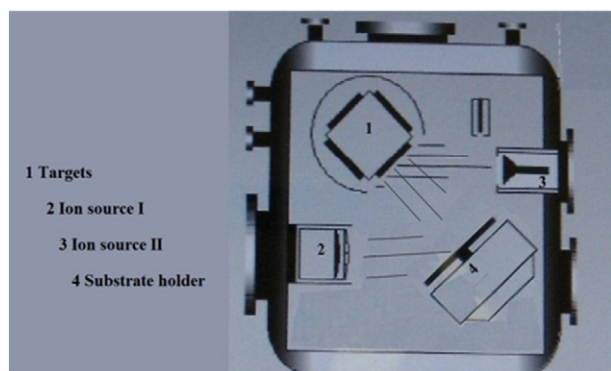


Fig. 1. Schematic of the BTIBD system.

high vacuum chamber, a pumping system, a power supply, and a computer control system. In the vacuum chamber, there are a target assembly, two ion sources (KRI EH-1000, manufactured by Kaufman & Robinson, Inc., USA), a substrate stage, shutters, and targets, as described in a previous work [12]. Fig. 1 presents a schematic diagram of the BTIBD system. B-DLC thin films were synthesized by simultaneously running the two EH-1000 ion sources, one for deposition of hydrogenated DLC with precursor gases methane (CH_4) and argon (Ar), and the other for B doping by sputtering a B_4C target of 99% purity. The deposition duration for the B-DLC film samples was 4 h achieving film thickness of approximately 0.24 μm . Pure hydrogenated DLC films and B-C thin films were also prepared by direct ion beam deposition and biased target sputtering of B_4C target with a fixed Ar gas flow rate of 50 sccm, respectively, as reference samples. P-type (100) mirror-polished 10 cm (diameter) silicon wafers were used as substrates. Prior to each thin film deposition, the substrate was chemically cleaned in an ultrasonic bath for 30 min with 95% ethyl alcohol and then placed into the vacuum chamber on the sample stage. The sample stage was located 300 mm away from the deposition ion source. It tilted 45° with respect to the deposition ion source and meantime rotated around its axis at a speed of 2 rpm for better film uniformity. The background pressure was 1.1×10^{-7} Torr and working pressure was 7.6×10^{-4} Torr. The substrate holder temperature was close to room temperature.

The surface morphology and cross-section of the synthesized film samples were observed using a scanning electron microscope (SEM, JEOL JSM-6010LV) operated at an accelerating voltage of 15 kV. An atomic force microscopy (AFM, PicoSPM) at the Saskatchewan Structural Science Centre (SSSC), University of Saskatchewan, was used to observe the surface topography of the synthesized films and to measure their surface roughness. An X-ray diffractometer (XRD, Rotaflex Ru-200) was used to characterize the crystal structure of the samples using $\text{Co K}\alpha$ line ($\lambda = 0.178897$ nm). Raman spectra of the synthesized films were obtained using a Renishaw 2000 micro-Raman system located at the SSSC, University of Saskatchewan and operated with an Ar ion laser of 514.5 nm wavelength. X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS) spectroscopy measurements were performed at the Canadian Light Source Inc. (CLS), University of Saskatchewan, using the Spherical Grating Monochromator (SGM) beam line and the Variable Line Spacing Plane Grating

Monochromator (VLS-PGM) beam line to study the chemical composition and elemental bonding states of the synthesized films. A Universal Mechanical Tester (UMT) manufactured by Center for Tribology Inc. was used to conduct nanoindentation testing and ball-on-disk friction testing to measure the hardness, elastic modulus and friction coefficient of the synthesized films.

3. Results and discussion

For B-C thin film deposition by biased target sputtering of B_4C target, both the target bias voltage and ion source anode current have effects on the sputtering rate, and thus the film deposition rate. The applied processing parameters, estimated film thickness and deposition rate are shown in Table 1. The mass of silicon wafers before (W_0) and after (W_i) film deposition was measured and recorded, respectively, as shown in Table 1. The weight increase ($W_i - W_0$) due to the deposition was used to estimate the film thickness (T). The deposition duration was set long enough for the accuracy of the measurements. Assuming the film density and silicon wafer area are ρ and a , respectively, we can estimate the average film thickness using $T = (W_i - W_0) / \rho a$. Then, the deposition rate (R) can be estimated by T divided by deposition duration. In those experiments, the area of silicon wafers is $\pi \cdot (5 \text{ cm})^2 = 78.5 \text{ cm}^2$, and the density of B_4C , $\rho = 2.5 \text{ g/cm}^3$, is used for the calculation. It can be seen that the deposition rate of B-C films increases with the increase of target bias voltage and ion source anode current, which is reasonable as sputtering rate increases with increasing sputtering ion energy and ion dose. Similarly, the deposition rate of pure hydrogenated DLC was estimated to be 53 nm/h under the applied processing parameters of maximum anode voltage setting of 150 V, anode current of 2.5 A, Ar flow rate of 10 sccm, and CH_4 flow rate of 6 sccm.

For B-DLC deposition, the processing parameters of deposition ion source were the same for pure DLC deposition. In order to prepare samples with different B contents, the processing parameters for sputtering of B_4C target (target bias voltage and anode current) varied as shown in Table 2. In this table, D.S. represents deposition source, which is the ion source for DLC deposition. Assuming the estimated deposition rate and the density of B_4C sputtered film and pure DLC film are $R_{\text{B}_4\text{C}}$, R_{DLC} and $\rho_{\text{B}_4\text{C}}$, ρ_{DLC} , respectively, then the B weight percentage in the synthesized B-DLC film can be estimated by $\text{B wt.}\% = [R_{\text{B}_4\text{C}} \cdot \rho_{\text{B}_4\text{C}} / (R_{\text{B}_4\text{C}} \cdot \rho_{\text{B}_4\text{C}} + R_{\text{DLC}} \cdot \rho_{\text{DLC}})] \cdot [4 \cdot 10.81 / (4 \cdot 10.81 + 12.01)]$, where 10.81 is B atomic weight and 12.01 is C atomic weight. $\rho_{\text{B}_4\text{C}} = 2.5 \text{ g/cm}^3$, $\rho_{\text{DLC}} = 2.2 \text{ g/cm}^3$, $R_{\text{DLC}} = 53 \text{ nm/h}$ and corresponding $R_{\text{B}_4\text{C}}$ in Table 1 were used for estimation of B concentration in B-DLC films. The estimated B wt.% is also shown in Table 2. The B weight percentage in the B-DLC films increases with the increase of target bias voltage and sputtering ion current and ranges from 2% to 8%.

Both the surface and cross-section of film samples were observed using SEM. The cross-section images of B-C film samples by sputtering B_4C are shown in Figs. 2 and 3. The films are dense and uniform with sharp interface to the substrates. The average film thickness obtained from the SEM observation is 0.73 μm for B-C-1 and 0.16 μm for B-C-3, respectively, which is slightly higher than that estimated by mass changes in Table 1. The film thickness of B-C-1 and B-C-4 was also measured by a profilometer and found to be averagely 654 nm and 96 nm respectively. These values are of higher accuracy comparing to those

Table 1
Sputtering parameters and estimated deposition rate on silicon.

Parameters/records	B ₄ C-1	B ₄ C-2	B ₄ C-3	B ₄ C-4	B ₄ C-5	B ₄ C-6
Target bias voltage (V)	800	100	400	400	400	200
Anode current (A)	4	4	4	2	1	4
Wafer mass before film deposition (W_0 , g)	9.30805	9.85130	9.84280	9.92090	9.72430	9.72550
Wafer mass after film deposition (W_i , g)	9.32010	9.85195	9.84510	9.92245	9.72535	9.72630
Deposition duration (h)	48	48	24	24	24	13
Film thickness (μm)	0.61	0.03	0.12	0.08	0.05	0.04
Deposition rate (nm/h)	13	1	5	3	2	3

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