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Deposition and characterization of diamond-like carbon films by microwave resonator microplasma at one atmosphere

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ABSTRACT

Diamond-like carbon (DLC) films have been deposited at atmospheric pressure by microwave-induced microplasma for the first time. Typical precursor gas mixtures are 250 ppm of C_2H_2 in atmospheric pressure He. Chemically resistant DLC films result if the Si (100) or glass substrate is in close contact with the microplasma, typically at a standoff distance of 0.26 mm. The films deposited under this condition have been characterized by various spectroscopic techniques. The presence of sp^3 C – H bonds and 'D' and 'G' bands were observed from FTIR and Raman spectroscopy, respectively. The surface morphology has been derived from SEM and AFM and shows columnar growth with column diameters of approximately 100 nm. Likely due to the low energy of ions striking the surface, the hardness and Young's modulus for the films were found to be 1.5 ± 0.3 GPa and 60 ± 15 GPa respectively with a film thickness of 2 μm. The hypothesis that a high flux of low energy ions can replace energetic ion bombardment is examined by probing the plasma. Rapid deposition rates of 4–7 μm per minute suggest that the method may be scalable to continuous coating systems.

1. Introduction

Diamond-like carbon (DLC) film plays a vital role in tribological applications because of its high hardness, good thermal conductivity, low friction coefficient, excellent wear resistance and chemical inertness [1–4]. These properties make DLC films suitable for numerous potential applications in hard and wear-resistant coating, lithography, hydrogen storage devices, optical coatings, field enhanced conductors and biomaterials. DLC films were first deposited by Aisenberg and Chabot [5] using ion beam deposition. There are various other techniques for the preparation of DLC films such as reactive magnetron sputtering [6], pulsed laser deposition [7], direct current plasma-enhanced chemical vapor deposition (PECVD) [8], electron cyclotron resonance microwave PECVD [9], dielectric barrier discharge [10] and radio frequency inductively coupled PECVD [11,12]. The properties of the DLC films vary considerably depending on the deposition techniques. In general, DLC films produced using low pressure techniques, for which energetic ion bombardment is typically encouraged by the application of large bias voltages, are comparatively harder (10–30 GPa) [13]. In contrast, DLC films deposited by high pressure dielectric-barrier discharges (DBDs) are comparatively less hard due in part to low energy ion fluxes (0.35–.92 GPa) [14].

In the current study we have used a cold, atmospheric pressure microplasma for the deposition of DLC films. The focus on atmospheric pressure seeks to eliminate vacuum components with a goal of simplicity and low cost. The microwave-induced plasma source is based on a microstrip split-ring resonator (SRR), for which a detailed description is reported elsewhere [15]. The potential advantage of using an SRR microplasma is its ability to create a steady-state ion density of ~10^{14} cm^{-3} while the gas temperature remains below 1000 K [16,17]. This density is several orders higher than the homogeneous DBD plasma which is limited to $\leq 10^{11}$ cm^{-3} [18]. We hypothesize that the high fluxes of low-energy helium ions (6×10^{17} cm^{-2} s^{-1}) and metastable species produced by the SRR microplasma will partially compensate for the absence of energetic ions, and improve the diamond-like properties of the films.

2. Experimental methods

2.1. Microplasma generation

The microplasma is formed using a microwave split ring resonator which is fabricated on Rogers Corp. TMM 10i laminate. This substrate material consists of a 2.5 mm thick dielectric (ceramic reinforced Teflon with a relative dielectric constant ε_r ~ 10) that was precoated with 17 μm thick copper on both sides. The ring-shaped microstrip pattern is defined in the top copper layer using a circuit board milling tool; the bottom copper layer remains intact and serves as a ground plane for the resonator. Microwave power is coupled into the microstrip and concentrated into a 200 μm gap which is formed in the ring. The electric field in the gap is sufficient to breakdown the flowing gas and to sustain

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an intense discharge. Information on the design and fabrication of the SRR is detailed elsewhere [15].

The microwave resonator is placed in a Plexiglas enclosure, as shown in Fig. 1a, with a volume of $6 \times 10 \times 10$ cm^3. Gas composition is controlled by two precision needle valves and the flow measured by two gas flow meters, one for a mixture of 1% acetylene by volume in He and a second for pure He. This configuration allows the careful control of acetylene concentration in the gas flow in the 25–10,000 ppm range. The gas flow is forced into the micro-discharge region through a 200 μm hole drilled through the SRR substrate in the middle of the discharge gap. This geometry results in stagnation point flow, with the maximum flow velocity near the center of the plasma and decreasing for larger radial distances.

The plasma power supply consists of a signal generator (HP 8656A, 0.1–990 MHz) and a power amplifier (ENI Model 525 LA), connected as shown in Fig. 1a. The power amplifier's output is sensed using a bidirectional coupler and power meter to measure the power in the forward traveling wave as well as the wave reflected from the plasma generator. As reported in this work, the power delivered to the generator is simply the difference between the forward and reflected power without minor corrections for cable loss. Typical conditions for a 3.5 W deposition are: forward power = 4.8 W, reflected power = 1.3 W at a frequency of 482 MHz.

Prior to each deposition, Si(100) or glass substrates were cleaned in isopropyl alcohol. Kapton spacers of the proper thickness were placed on the SRR surrounding the microplasma region. The substrate was then placed face down on the Kapton spacers, as shown in Fig. 1b. This method consistently sets the spacing between the microplasma and the substrate. Prior to each deposition the plasma enclosure was purged by a continuous flow of pure He gas for about 3-4 minutes with a flow rate of 1000 sccm. Power was next applied to the SRR and the discharge was allowed to stabilize for a few seconds. Then the appropriate flow of He^+ 1% C_2H_2 is introduced to initiate deposition. Once the deposition period is completed, the experiment is halted by turning off the microwave power.

2.2. Ion flux

The ion flux in the microplasma was probed without a substrate by inserting an unbiased stainless steel wire into the plasma and measuring the resulting electrical current through a grounded 43 kΩ resistance. Although the discharge gap is 200 μm, the actual plasma size expands to

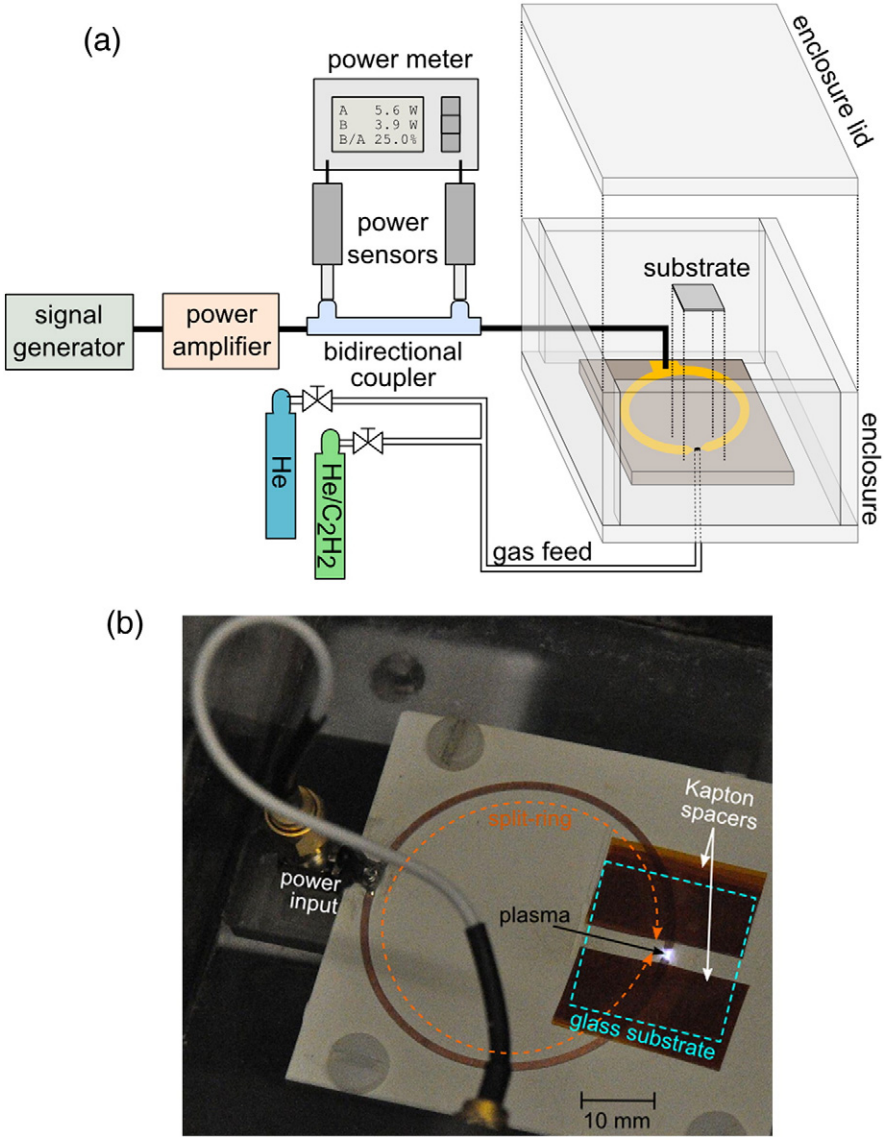

Fig. 1. (a) Schematic experimental setup of the deposition system and (b) a photograph of an SRR microplasma as viewed through a glass substrate with DLC deposition in progress.