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Ion beam deposition of DLC and nitrogen doped DLC thin films for enhanced haemocompatibility on PTFE

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ABSTRACT

Diamond-like carbon (DLC) and N-doped DLC (DLC:N) thin films have been synthesized on polytetrafluroethylene (PTFE) and silicon wafers using ion beam deposition. Raman spectroscopy, atomic force microscopy, X-ray photoelectron spectroscopy and scanning electron microscopy were used to study the structural and morphological properties of the coated surface. The results show that the ion beam deposited DLC thin films exhibit high hardness and Young's modulus, low coefficient of friction and high adhesion to the substrate. Low concentration of nitrogen doping in DLC improves the mechanical properties and reduces the surface roughness. DLC coating decreases the surface energy and improves the wettability of PTFE. The platelet adhesion results show that the haemocompatibility of DLC coated PTFE, especially DLC:N coated PTFE, has been significantly enhanced as compared with uncoated PTFE. SEM observations show that the platelet reaction on the DLC and DLC:N coated PTFE was minimized as the platelets were much less aggregated and activated.

1. Introduction

Synthesized vascular grafts are now made mainly from extruded polytetrafluoroethylene (PTFE). The artificial small vessels constructed from PTFE are the only alternative to autologous implants for more than 500,000 patients requiring coronary artery bypass surgery and more than 150,000 patients for lower limb surgical replacement operations annually in the United States. Polymers possess many desirable properties for biomedical applications, including a density comparable to human tissues, good fracture toughness, resistant to corrosion, and ease of forming by molding or machining and are increasingly chosen as a material in a variety of implants for widespread applications. However, PTFE polymers do not possess desirable heamocompatibility and often result in thrombus formation when in contact with blood.

Diamond-like carbon (DLC) thin films exhibit excellent biocompatibility, high hardness, high chemical inertness, high wear and corrosion resistance, and very low coefficient of friction, which make this material ideal as coatings for biomedical implants [1,2]. DLC has been demonstrated to be biocompatible *in vitro* and *in vivo* in orthopedic applications. Coating polymer-based biomedical devices, such as blood vessels, heart valves, and coronary stents with DLC thin films, is expected to significantly improve not only their haemocompatibility but also tribological performance and lifetime. However, DLC films are always accompanied by a high internal compressive stress due to the ion bombardment during the deposition, which limits their possible applications. Recently, Silva et al. [3] investigated the effects of nitrogen doping on properties of DLC films and showed a clear reduction of the internal compressive stress without significant changes in other properties upon nitrogen doping. Zheng et al. [4] found that DLC coating significantly improved the heamocompatibility of NiTi alloy and 316L stainless steel; the blood clotting time increases and amount of platelets decreases as the surface roughness of the DLC coatings decreases; and the increase in nitrogen concentration of the film has resulted in decrease in the platelet adhesion. Therefore, DLC and nitrogen doped DLC (DLC:N) films are promising to be used as coatings on PTFE to improve its heamocompatibility. However, the structure and the heamocompatibility of ion beam deposited DLC and DLC:N coating on PTFE have not been fully investigated as required for practical applications.

The objective of this work is to develop an ion beam assisted deposition process to synthesize DLC and DLC:N thin films on PTFE in order to enhance the heamocompatibility of artificial vascular graft made from PTFE. The microstructure, mechanical properties, and haemcompatibility of the DLC and DLC:N thin films on PTFE have been investigated.

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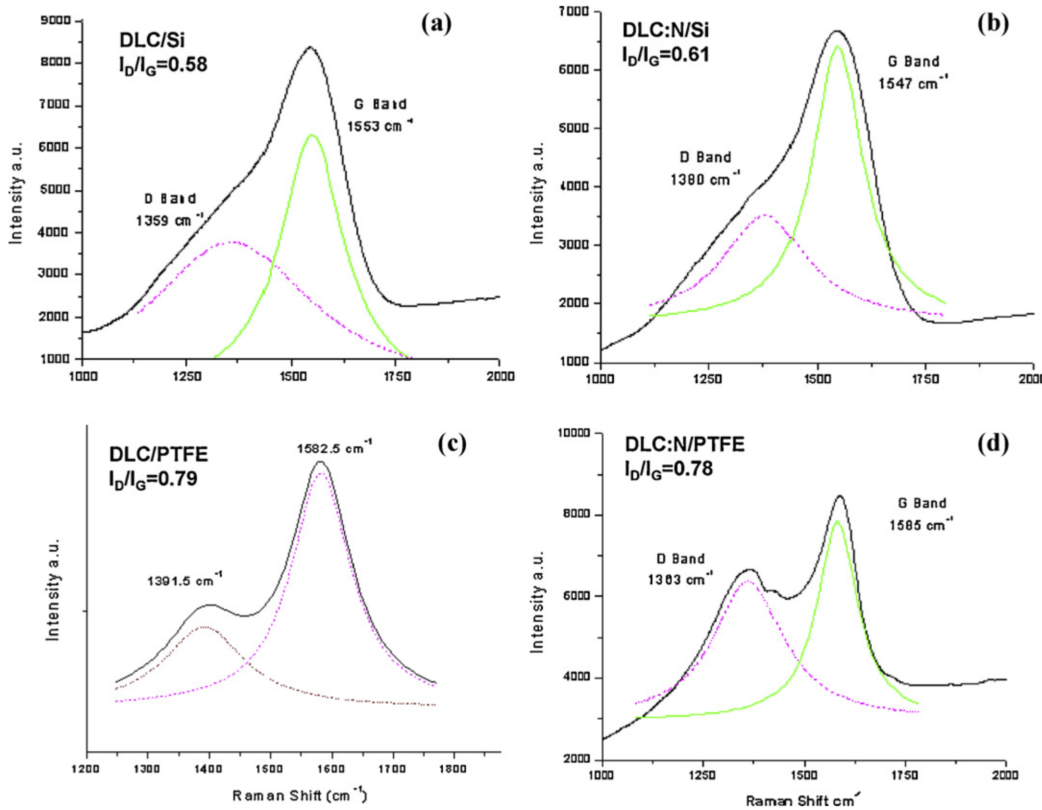

Fig. 1. Raman spectra of (a) DLC and (b) DLC:N on Si and (c) DLC and (d) DLC:N on PTFE.

2. Experimentals

2.1. Ion beam deposition of DLC thin films

DLC thin films were synthesized by an ion beam deposition system manufactured by 4wave Inc. It uses a Kaufman-type ion source for direct ion beam deposition. The substrate stage faces to the ion source and is cooled by water. The configuration of the coating system has been described elsewhere [5]. Mixture of methane and argon were used as precursor. The DLC thin films were synthesized with energies of 250–300 eV and a beam current of 75 mA. Prior to commencing the deposition, PTFE sheets and Si wafers as substrates were Ar^+ ion sputter cleaned with beam energy of 800 eV for 15 min. During the DLC deposition, high purity methane and argon with flow rate of 8 and 24 sccm, respectively, were ionized simultaneously in the ion source and directed toward the substrate. For synthesizing DLC:N thin films, 2 sccm N_2 was added. The base pressure was 5×10^{-7} torr and working pressure was 7×10^{-4} torr. All depositions were made at room temperature. All the films were deposited for 4 h to ensure sufficient thin film thickness for investigations of structures and properties including haemocompatibility.

2.2. Structural characterization

Raman spectra were measured using a Renishaw system (model 2000) operated at 514 nm Ar ion laser with a spot size of approximately 2 μm. Three spots were chosen to obtain Raman spectra for each sample. XPS measurements were performed at SGM beamline at Canadian Light Source (CLS), University of Saskatchewan, using synchrotron X-ray source simulated to Mg K-α at 1260 eV photon energy. Peak areas were measured, and divided by the atomic sensitivity factors [6] to calculate film composition.

2.3. Mechanical property characterization

Mechanical properties of DLC films coated on Si substrates were measured by nano-indentation using a Universal Materials Tester (UMT) manufactured by Center for Tribology (CETR) Inc. A Berkovich type indenter tip was used for the nano-indentation testing. The nano-indentation testing was conducted in three different locations for each sample. The maximum load was 5 mN. For each loading/unloading cycle on each spot, the applied load value is plotted with respect to the corresponding position of the indenter. Film hardness and Young's modulus were calculated from the resulting load/displacement curves based on the Oliver and Pharr method [7].

2.4. Contact angle and surface energy

The contact angles of PTFE substrates with and without DLC coatings were quantified by measuring static water contact angle. They were measured from the profiles of liquid distilled water drops placed on the samples at room temperature. The values of the water contact angle are average from two samples. Static contact angles were measured with a microscope equipped with CCD-video, prism and stand with tiltable plane. Pictures taken by this method were analyzed using image processing program. The accuracy of the contact angle measurements was 1°. Surface energy can be calculated by using Young–Dupre equation $E = \gamma(1 + \cos\theta)$ where γ is the surface tension of water at 20 °C (γ = 72.8 mN/m) and θ is the contact angle (°)

2.5. Haemocompatibility testing

Blood was collected from a healthy donor who was under no medication for at least 10 days prior to the donation and was collected in tubes containing anticoagulants. Small amount of