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Molecular structure of SiO_x-incorporated diamond-like carbon films; evidence for phase segregation

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ABSTRACT

Silicon-oxide incorporated amorphous hydrogenated diamond-like carbon films (SiO_x–DLC, $1 \le x \le 1.5$) containing up to 24 at.% of Si (H is excluded from the atomic percentage calculations reported here) were prepared using pulsed direct current plasma-enhanced chemical vapour deposition (DC-PECVD). Molecular structure, optical properties and mechanical properties of these films were assessed as a function of Si concentration. The spectroscopic results indicated two structural regimes. First, for Si contents up to ~13 at.%, SiO_x–DLC is formed as a single phase with siloxane, O–Si–C_2, bonding networks. Second, for films with Si concentrations greater than 13 at.%, SiO_x–DLC with siloxane bonding and SiO_x deposit simultaneously as segregated phases. The variations in mechanical properties and optical properties as a function of Si content are consistent with the above changes in the film composition.

1. Introduction

There has been a considerable effort for modifying the properties of amorphous hydrogenated diamond-like carbon (DLC) films by doping with various elements including H, N, Si, F, Ti, W, Ca, P and others. The diamond-like structure in DLC is derived from the significant presence of sp^3 bonding. Such films have many properties similar to that of diamond [1]. However the high residual stress and low thermal stability in air are some drawbacks which prevent wider practical use of this material. By introducing dopants, the chemical structure of DLC may be modified for example, by altering the sp^3 *to* sp^2 ratio in carbon bonding. These changes in chemical bonding transform film properties such as hardness, stress, coefficient of friction, thermal stability, hydrophilicty, bioactivity and others which may suit different applications [2–4].

Doping of DLC with Si has been widely studied [5–13]. Si is generally bonded to four carbon atoms and there is evidence for substantial changes in surface and bulk properties. SiO_x doped DLC (SiO_x–DLC) has been synthesised using ion beam assisted deposition [14] and radio frequency glow discharge reactors [15–18]. These studies have focussed on tribological, structural, chemical and surface properties of SiO_x–DLC films as a function of various experimental parameters and composition. The general consensus is that the films are dominated by Si–O networks and carbon networks with Si–C bonding with some evidence for phase segregation [15,18–20]. To our knowledge, SiO_x–DLC films have not been prepared using a pulsed direct-current plasma enhanced chemical vapour deposition (DC-PECVD) technique. This technique has advantages over the conventional radio-frequency (RF) methods in that it is more readily adapted to industrial-scale applications. Understanding of how the differences in the chemical structure of films prepared using various deposition techniques influence the resulting mechanical, biomedical and electronic properties is an integral part of the ongoing research into the applications of thin films in industry. In this paper we present an analysis of the molecular structure and composition of SiO_x–DLC films synthesised using DC PECVD technique and compare them to Si–DLC films.

2. Experimental

A schematic of the DC-PECVD deposition system is shown in Fig. 1 and has been described in detail elsewhere [5,21]. The substrate electrode inside of the stainless-steel chamber was powered by a direct current (DC) pulse generator (Rübig Model MP120) operated at 415 V. The semiconductor-grade silicon (100) substrates were firmly secured onto a steel disc fitted to the end of the Cu electrode (see Fig. 1). The gases were introduced into the chamber through a gas distributor using mass flow controllers (MFCs). The pressure inside the chamber was maintained at 185 Pa (measured by a capacitance manometer) with the aid of a pumping system equipped with a throttle valve.

The preparation of Si–DLC films using tetramethylsilane (TMS) is described elsewhere [5] and the following details apply for the preparation of SiO_x–DLC films. The glass vessel containing the metal-organic precursor, tetraethoxysilane (TEOS, $(C_2H_5O)_4Si$, Sigma Aldrich 98%), was heated to 50 °C–70 °C in a water bath. Argon was used as the carrier gas for the liquid precursor. The stainless steel tubing connecting the glass vessel containing the liquid precursor to the

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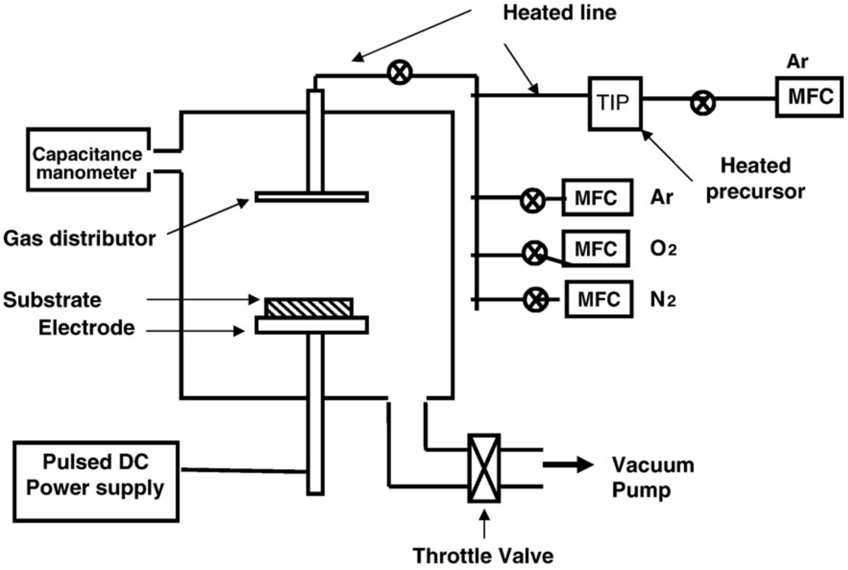

Fig. 1. A schematic of the pulsed DC-PECVD apparatus used for the syntheses of DLC and modified DLC films.

chamber was heated to 70–90 °C to prevent condensation. Flow of TEOS was controlled by a needle valve to obtain DLC films with varying amounts of SiO_x. Typical flow rates for experiments are shown in Table 1. Depending on the required thickness of the film, the deposition time varied from 15 min to 20 min.

The composition of the films was determined by X-ray photoelectron spectroscopy (XPS) in a SPECS150 system operated with Mg K_αX-ray source (10 keV and 10 mA) [22]. The peaks were referenced to the adventitious C *1s* peak at 284.6 eV to compensate for surface charging. The fitting of the peaks using a Gaussian/Lorentzian product formula with a Shirley background [23] was carried out using CASA-XPS V2.3.13 software. Fourier Transform Infra Red (FTIR) spectrometry was performed using a Digilab FTS40 Spectrometer with a glow bar source, a KBr beam-splitter and a liquid nitrogen-cooled MCT detector. The spectrometer was equipped with a Model 091-0608A universal sampling accessory to allow diffuse reflectance measurements in the mid-infrared (400 to 6000 cm^{-1}, or 1.7 to 25 µm). Raman spectroscopy was performed using Renishaw *In Via* confocal Raman microscope system. Specimens were illuminated with 514 nm excitation from an Ar^+ laser at an incident power of ~1 mW and a spot diameter size of approximately 1 µ. The ellipsometric parameters of the films were measured with a custom-made rotating spectroscopic ellipsometer [24]. These parameters were used to calculate the optical constants [25]. We have applied the effective medium approximation (EMA) layer model (used for mixed layers) to calculate the optical properties (refractive index and the extinction coefficient) of various films with varying SiO_x and DLC contents. This model is commonly used for mixed material as in this study. The optical data are treated by adjusting the DLC and SiO_x compositions using a least-squares method within the EMA approximation. The optical band gaps, E_T were determined from the extinction coefficients using the Tauc approach [26]. In this approach, E_T is given by the intercept of the extrapolated linear fit to a plot of ($\alpha h\upsilon$ versus photon energy, $h\upsilon$. Here, h is the Planck's constant; υ is the frequency of radiation and α is the absorption coefficient. The film thickness was measured using a step-edge profilometer (Sloane Instruments Dektak 3030). The hardness of the films was measured with a UMIS 2000 ultra micro-indentation system fitted with a diamond Berkovich indenter. Tests over a load range of 1 to 10 mN suggested an optimum indentation load of 5 mN. The residual stress in the films was determined by measuring the radius of curvature of the substrate before and after deposition using the profilometer.

3. Results and discussion

Using the experimental method discussed above, robust SiO_x–DLC films were obtained at typical deposition rates of 60–70 nm/min. The thickness of the films examined in this paper is approximately 1 µm. Varying amounts of SiO_x were incorporated into the films by changing the flow rate of TEOS. For comparison purposes, Si–DLC films of a similar thickness were grown using the pulsed DC PECVD method, as described in an earlier publication [5].

4. XPS results

Both SiO_x–DLC and Si–DLC films with Si concentrations of 5 to 24 at.% were obtained by the pulsed DC PECVD technique. Although the hydrogen content could not be determined directly from XPS, estimates of H concentrations are made using the photoluminescence background of the Raman spectra (see below). The atomic percentages reported throughout the manuscript for Si, O and C are those determined by XPS and exclude the presence of H. In Fig. 2 we show the XPS spectra for Si *2p*, C *1s* and O *1s* core electrons for SiO_x–DLC films (three upper panels) and for Si–DLC films (three lower panels) which contain 22 at.% of Si. Consider first the Si *2p* peaks. For Si–DLC films, for all concentrations of Si, the peaks for Si *2p* can be resolved into two contributions, one at 100.4 ± 0.1 eV (80 –90% peak area) and another at 101.3 ± 0.3 eV (10 – 20% peak area). The peak at lower binding energy is consistent with silicon carbide bonds. The one with higher binding energy most likely arises from the presence of Si bonded to O. Substitution of a carbon atom with a more electronegative oxygen atom causes the Si *2p* peak to shift to higher binding energy. Since there is no oxygen present in the TMS, it is most likely that such oxygen containing structures in Si–DLC films are confined to the surface. This assertion is supported by the FTIR data discussed below. No changes were observed for the Si *2p* binding energies within the range of Si concentrations from 4 at.% to 24at.%. Therefore, as the Si concentration is increased, the chemical environment of Si remains the same.

Table 1
Typical flow conditions used for the SiO_x–DLC film deposition (sccm/min).

Ar	H_2	CH_4	Ar/TEOS
80	45	45	2–5