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Structure and characterization of the multilayered Ti-DLC films by FCVA

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ABSTRACT

This work presents a simple approach for the synthesis of multilayered titanium-diamond-like carbon (multilayered Ti-DLC) films on a Si substrate by a filtered cathodic vacuum arc (FCVA) system using Ti-coated graphite target to supply carbon as well as the dopant titanium. This study focuses on the characterization of microstructure, surface roughness, mechanical strength and electrical resistivity. The results indicated that the multilayered Ti-DLC films exhibit better mechanical properties than the Ti-free and Ti-implanted DLC films, and both multilayered Ti- and Ti-implanted DLC films have similar Ti atomic concentrations. The surface roughness of the multilayered Ti-DLC films shows a value much lower than the other films. The film microstructure consists in TiC nanocrystals precipitated in the amorphous carbon matrix with a multilayered structure. Because of the high hardness and low roughness, the multilayered Ti-DLC films can be used as biomedical, wear-resistant and solid lubricant coatings.

1. Introduction

Diamond-like carbon (DLC) film is a meta-stable form of amorphous carbon with high fractions of sp^3 bonds, which has stimulated a great deal of interest due to their superior physical and chemical properties, such as high hardness, low friction coefficient, chemical inertness, optical transparency, thermal conductivity and biocompatibility [1–7]. Doping with appropriate atoms is well known to alter and modify the optical, electrical and mechanical properties [8–21].

It has been well known that metals can be incorporated into DLC films by various methods, including sputtering deposition [20,21], metal vapor vacuum arc [17] and plasma sources implantation [22,23]. For sputtering deposition, metal is incorporated into DLC films by sputtering a metal target, and the doped metal content is therefore controlled by changing the fraction of the precursor gas (such as CH_4 or C_2H_6). However, the low-energy sputtered atoms result in the low-density films with a large amount of graphitic bonds [20,21]. For the ion-implantation methods, such as metal vapor vacuum arc and plasma source implantation, the metal ions are incorporated into an amorphous carbon matrix following the bombardment with highly energetic positive ions. This process is efficient and low-cost and has industrial applications [17,22,23]. However, the hardness of the films is therefore reduced due to the damage produced by the highly energetic ion bombardment [17].

This work develops a new approach for synthesizing self-assembled multilayered Ti-DLC films. The Ti-DLC films are deposited on a Si substrate using the FCVA system with a Ti-coated graphite target, serving as carbon and Ti source. The structure of the films is often multilayered and formed by moving the arc spot toward the surface with a low electrical resistivity. The resulting multilayered Ti-DLC films have a much lower surface roughness (~0.107 nm) with a super hardness (~57 GPa) than the Ti-free DLC (~36 GPa) and the metal-doped DLC films (~30 GPa) using other methods. The as-prepared Ti-DLC films exhibit a super mechanical strength with a very low surface roughness, indicating that the multilayered Ti-DLC films have potential applications for protective, hard and lubricating coatings.

2. Experimental details

2.1. Film synthesis and annealing treatments

The multilayered Ti-DLC films with a thickness of 150 nm were deposited on a Si substrate (2×2 cm^2; p-type) under a dc pulsed negative bias of −300 V at 25 kHz with a duty cycle of 50% in a 90°-bend magnetic FCVA system. Before synthesizing the multilayered Ti-DLC films, a Ti film of 2 and 5 μm, acting as Ti sources were deposited on a graphite target (99.999% pure; 4 in. in diameter). The high-density plasma can be obtained from such a Ti-coated graphite target in an atmosphere of 9.3×10^{-2} Pa. The main arc was initiated using a Mo trigger to start the pulses, and maintained by the main arc pulse until it's shut-off. All the neutral atoms and macroparticles were filtered out by the magnetic filter with a curved axial field [24]. During the deposition of the DLC films, the working pressure of the vacuum chamber and the substrate temperature were maintained at 9.3×10^{-2} Pa and 300 K for 3 min. For comparison, the Ti-free DLC films were prepared using a pure

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graphite target; the Ti-implanted DLC films were then synthesized using metal vapor vacuum arc (MeVVA) Ti ion sources. The implantation dosage was fixed at 1×10^{17} ions/cm^2 with an accelerating voltage of 30 kV.

2.2. Characterization, hardness and electrical resistivity of Ti-DLC films

The elemental compositions and chemical bonding of the multilayered Ti-DLC films were investigated by X-ray photoelectron spectroscopy (XPS Perkin-Elmer Model PHI1600 system) using a single Mg–K_α (1253.6 eV) X-ray source, operated at 250 W. The depth profiles of the films were measured by nano-Auger electron spectroscopy (nano-AES Auger 700 PHI Xi, Physical Electronics). The cross-section view and high resolution transmission electron microscopy (HRTEM) images of thin films were observed by the transmission electron microscopy (JEOL TEM 2010, 200 kV). The microstructure of the film was analyzed by a micro-Raman spectroscope, with an excitation at the 632.8 nm (1.96 eV) line of an He–Ne laser. The surface morphology and roughness of the deposited films were observed over an area of 1 μm × 1 μm by an atomic force microscope (AFM, Digital Instrument NS3a Controller with D3100 Stage) in tapping mode. The electrical resistivity of the Ti-DLC films was measured using a four-point probe technique. Finally, the hardness of the Ti-DLC films was measured by the nano-indentation (XP nano-mechanical testing system, MTS Corporation) with a maximum force of 1 mN, using a Berkovich diamond indenter. The measurement was operated under the continuous stiffness measurement (CSM) mode, and the indentation depths were maintained at one tenth of the thickness of the film to prevent any substrate effect.

3. Results and discussion

3.1. Chemical composition and bonding

Fig. 1 shows the C 1s and Ti 2p core-level spectra of the Ti-DLC films with three titanium contents of 0, 1.08 and 4.10 at.%. The atomic percentage of Ti in the Ti-DLC films is determined as the ratio of the area under the C 1s peak to that under the Ti 2p peak in the XPS core-level spectrum, corrected by the atomic sensitivity factors (C: 0.314 and Ti: 2.077). The Ti contents of the Ti-DLC films were found to be proportional to the thickness of the Ti films that was deposited on the graphite target for the making of the Ti-DLC films. A thicker Ti coating always yields a higher Ti content of the Ti-DLC film, but when a Ti-free graphite target was used, nothing but Ti-free DLC films were formed. In Fig. 1(a), the C 1s core-level spectra include five peaks, corresponding to C–O at 288.4 eV, sp^2 carbon satellite peak at 286.5 eV, sp^3 bonded carbon at 285.2 eV, sp^2-bonded carbon at 284.3 eV and TiC at 282 eV, respectively [25,26]. The sp^2/sp^3 ratios of the DLC films with three titanium contents of 0, 1.08 and 4.10 at.% are 0.72, 2.42 and 4.24, respectively, which reveals that the sp^2/sp^3 ratio increases with increasing Ti content of the as-prepared DLC films. Also, the formation of C–Ti bonds clearly reveals that the Ti-DLC films can be successfully prepared by this method. As shown in Fig. 1(b), the appearance of the Ti 2p 3/2 peak at 461.5 eV and the Ti 2p 1/2 peak at 456.2 eV also indicates that the Ti ions have been added into the films. Moreover, the relative intensity of the C–Ti bonds increases with the Ti content from 0 to 4.10 at.% [Fig. 1(b)].

3.2. Depth profiles

Fig. 2 illustrates the nano-AES depth distribution of Ti atoms in the Ti-DLC films, which shows the alternate rise and fall of the Ti

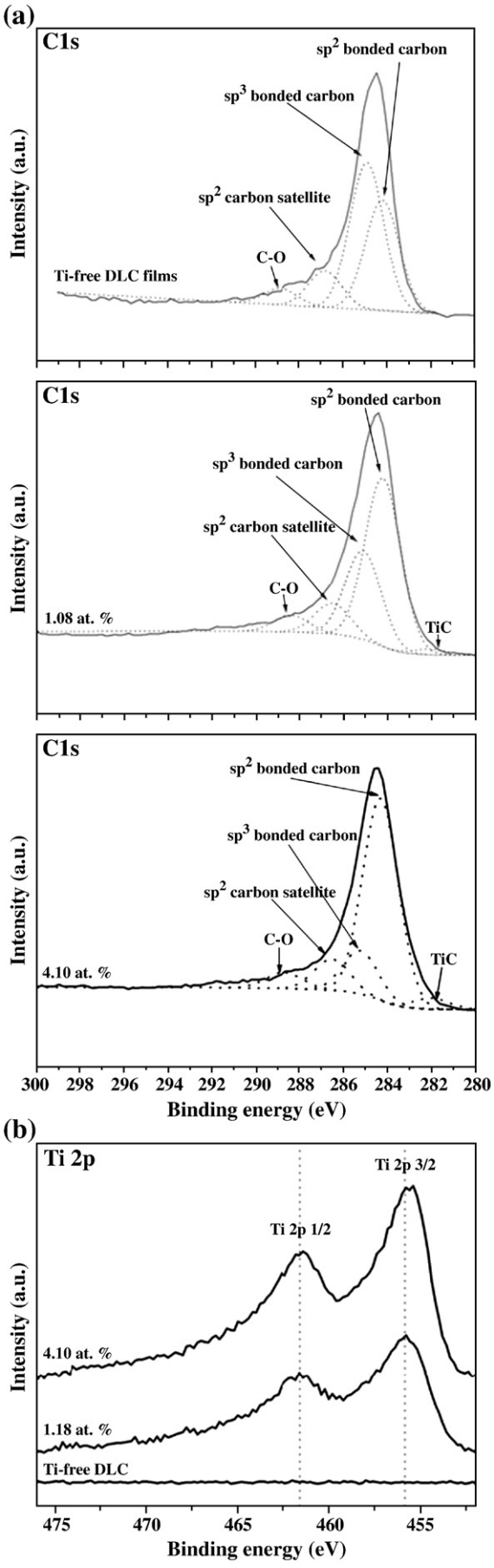

Fig. 1. XPS core-level spectra of the multilayered Ti-DLC films with varying Ti concentration of 0, 1.08 and 4.10 at.%: (a) C1s, and (b) Ti2p.