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Deposition and microstructure of Ti-containing diamond-like carbon nanocomposite films

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Abstract

Ti-containing diamond-like carbon (DLC) films were deposited by plasma decomposition of CH_4/Ar gas mixtures with an introduction of tetrakis(dimethylamino)titanium (TDMAT, $Ti[(CH_3)_2N]_4$), which was used as a precursor of titanium. The films deposited were found to be nanocomposite coatings consisting of TiN nanocrystalline clusters and amorphous hydrocarbon (a-C:H), indicating that the nanocrystalline clusters were embedded in the DLC matrix. The crystallinity of TiN clusters, as well as the Ti atomic concentrations in the films, increased with an increase of substrate temperature. The substrate temperature applied to form a crystalline phase in the DLC matrix induced a graphitization of amorphous hydrocarbon matrix. The increase of volume fraction of TiN nanocrystalline clusters in the DLC matrix enhanced the mechanical properties of nanostructured coatings, although the graphite-like structural transition of DLC matrix happened due to the applied heating.

Keywords: Diamond-like carbon; Nanostructures; Metal–organic precursor; Hardness

1. Introduction

Amorphous hydrogenated carbon (a-C:H), also called diamond-like carbon (DLC), have been a special issue among the carbon-based materials because it has favorable properties such as high hardness, low friction coefficient, high wear resistance, optical transparency and chemical inertness. Although the DLC films have poorer physical properties than diamond films, they provide interesting features: deposition at room temperature and superior surface roughness. However, a limited number of industrial applications of DLC coatings were taken due to their low thermal stability, high internal residual stress and environmental dependence of the wear properties. Third elements incorporation such as silicon, nitrogen and some metals has been considered to solve the problems of DLC coatings [1–5].

Nanostructured materials have received much attention because of their potential of synthesizing materials with unique properties [6–9]. The development of protective coatings aiming at a combination of advantageous material properties such as enhanced hardness, wear resistance and chemical stability has been achieved through the design of nanostructured coatings. There are many kinds of nanostructured coatings design such as nanocomposite coatings, nanoscale multilayer coatings, nanoscale-graded coatings, etc. [10]. The development of nanostructured films is required for the progressive improvement of hard coating materials. The nanoscale design of coating materials is usually achieved by means of nanocomposite and nanomultilayer films [10].

Metal-containing amorphous hydrocarbon coatings have been studied for several years [11–15]. DLC coatings with a metal greater than a few atomic percentages have exhibited nanostructured characteristics composed of nanocrystalline clusters in an amorphous matrix [13–15]. In these coating systems, the hardness enhancements were found as the

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metal concentration in the films increased. Such nanostructured DLC coatings were usually deposited by a combined plasma-assisted physical vapor deposition/chemical vapor deposition technique and sputtering system [13–15]. The metal incorporation into the DLC matrix has been usually achieved by sputtering the metal target. The metal content in the film can be usually adjusted by the variation of hydrocarbon to inert gas (for target sputtering) ratio. However, following disadvantageous effects should be considered in such a sputter-based deposition system. The films with a relatively high graphitic bond can grow by sputtering due to the low energy of the sputtered atoms, resulting in less-dense films [16]. Amorphous hydrocarbon films can be also deposited onto the metal target especially at a high hydrocarbon to inert gas ratio because the target is usually attached to the biased cathode. This so-called target poisoning could result in the reduction of metal content in the films with an increase of process time [17].

In plasma-enhanced chemical vapor deposition (PECVD) system, the metal incorporation can be achieved by an introduction of additional gaseous precursor, which could be easily made by the vaporization of metal–organic precursors. Furthermore, the system simplicity in this process is possible because of no need of sputter system for the metal incorporation. In the present study, we applied the metal–organic precursor for the Ti incorporation into the DLC films. Ti-containing DLC films were deposited by plasma decomposition of Ar/CH_4 gas mixtures with an introduction of tetrakis(dimethylamino)titanium (TDMAT, $Ti[(CH_3)_2N]_4$), which was used as a precursor of titanium. The formation of nanocrystalline phases in the DLC films and structural modifications of the DLC matrix were monitored as a function of substrate temperature and Ti atomic concentrations. The synthesis, microstructure and mechanical property relationship of nanostructured DLC coatings grown by PECVD were investigated.

2. Experimental details

The PECVD system used in this study consisted of a capacitively coupled, asymmetric plasma reactor driven by a 13.56 MHz rf power supply which was connected to the lower electrode. A self-biased negative voltage ($-V_{dc}$) was developed at the powered electrode due to the asymmetry between upper and lower electrode and also a large difference in the electron and ion mobilities. The reactor was evacuated by a combination of a mechanical rotary pump and a turbo-molecular pump. The source gases were uniformly distributed by a showerhead type distributor. A bubbler system was used to supply liquid sources to the reactor. The bubbler containing a liquid precursor was encapsulated with a band heater. The gas line was also tapped with a line heater to prevent any condensation during the delivering of vaporized precursor to the reactor. Si (100) wafers were used as substrates, which were placed on the lower electrode. Methane (CH_4) and TDMAT were used as precursors of C and Ti, respectively. TDMAT was supplied to the reactor by N_2 gas flow. The flow rate of carrier N_2 gas was fixed at 10 sccm and the temperature of bubbler containing TDMAT was fixed at 60–65 °C. The vapor pressure of liquid source at this temperature was approximately 133 – 173 Pa. The flow rate of CH_4 gas was fixed at 20 sccm. The negative bias voltage was fixed at 200 V. The substrate temperatures were varied from room temperature to 500 °C, which were controlled by additional resistant heater equipped at the lower electrode and ion bombardment to the lower electrode of precursor ions. The base pressure was less than 6.6×10^{-4} Pa and working pressure was kept between 16 – 20 Pa. Before being loaded in the CVD chamber, Si substrates were ultrasonically cleaned in acetone and ethanol, respectively. Then, they were rinsed in DI water. Finally, Si substrates were exposed to Ar plasma to clean the surface.

The film thickness was determined by cross-sectional view in scanning electron microscope (SEM, Hitachi S-5000). All the coatings had a thickness ranging from 450 to 500 nm, independent of substrate temperatures. The chemical composition of the films grown was determined by Auger Electron Microscopy (AES), with Ar ions depth profiling using a PHI 680 Auger Nanoprobe. The base pressure in AES chamber was less than 1.33×10^{-8} Pa, and the chamber pressure during Ar ions sputtering was approximately 1.33×10^{-6} Pa. The incident beam current and beam voltage were 10 nA and 10 kV, respectively. The beam voltage and emission current for Ar ion gun were 3 kV and 15 mA, respectively. The binding energy of titanium, carbon and nitrogen in the coatings was monitored by X-ray photoelectron spectroscope (XPS, VG Microtech) to investigate the bonding state in the coatings. XPS measurement was carried out using Al Ka radiation, with an energy of 1486.6 eV. The base pressure in XPS chamber was less than 1.33×10^{-7} Pa, and the chamber pressure during the XPS survey was approximately 1.33×10^{-6} Pa. The crystalline phases in the films were examined by X-ray diffraction (XRD, Bruker D8 Discover) using Cu Ka radiation. The diffraction patterns were obtained by 2θ scan at a fixed incident angle. Transmission electron microscope (TEM, Hitachi H-8000), operated at 200 kV, was also employed to identify the crystalline phases in the films. The TEM specimens for the cross-sectional view were prepared by a typical procedure followed by polishing, grinding and ion milling. Raman spectrometer (Jobin-Yvon, T64000) was employed to investigate the chemical structure of amorphous carbon matrix. Raman spectra were obtained in a backscattering geometry using Ar ion laser excited by the 514.5 nm lights. The spectra in the wave number ranging from 1000 to 1800 cm^{-1} were fitted by so-called D and G peaks [18] using Gaussian-curve function. The hardness and elastic modulus of grown films were evaluated using an ultra microindentation system (UMIS-2000) equipped with a diamond indenter. The indentation tests were performed