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# The study of doped DLC films by Ti ion implantation

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**Abstract**

Diamond-like carbon (DLC) films were prepared by unbalanced magnetron sputtering. Ti-doped DLC films were obtained by Ti ion implanted into the achieved DLC films using metal vapor vacuum arc (MEVVA). The effects of $Ti^+$ ion implantation on the surface morphology, structure, and tribological properties of the DLC films were investigated by means of atomic force microscopy (AFM), Raman spectroscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and friction measurement. The smooth and uniform Ti-doped film with the surface roughness of 0.595 nm was obtained. Raman result revealed that the formation of DLC films and $sp^2$ bonds content increase by $Ti^+$ ion implantation. TEM showed that the nanocrystalline phases of TiC were formed in the films. $Ti^+$ was implanted into the interface between C and substrate, detecting the sputtering depth profiles of the film by XPS; thus, the interface was widened due to reserve diffusion. Tribological test experiment indicated that friction coefficient of the films decreased to approximately 0.15 by $Ti^+$ ion implantation.


*Keywords:* Diamond-like carbon films; Ion implantation; Ti doped

## 1. Introduction

Diamond-like carbon (DLC) film is an amorphous carbon material containing a significant fraction of $sp^3$ bonds. DLC films have stimulated great interests due to relatively simple preparation and extraordinary properties similar to diamond, including high hardness, low friction coefficient, high wear resistance, chemical inertness, optical transparency, and thermal conductivity [1,2]. The studies of DLC films have been performed extensively since 1971, when Aisenberg and Chabor [3] first prepared such films by using ion beam deposition. The films can be synthesized by magnetron sputtering, laser ablation, cathodic arc evaporation, ion beam deposition, and electrochemical deposition. The film characteristics depend on several different deposition process parameters, such as gas composition and pressure, substrate temperature, energy of the impinging ions, etc. As a result, the mechanical and tribological properties of the DLC films may differ from one study to another.

The incorporation of other elements [4,5] into the DLC films provides a way to improve the properties of the films. Ion implantation is commonly used as the method to modify surface properties of materials, such as corrosion resistance, tribological applications, and semiconductor applications. A new type of metal arc ion source, namely metal vapor vacuum arc (MEVVA), has been recently used in plasma ion implantation. This source, developed by Brown et al., has a broad beam and high current capabilities.

In the present paper, titanium has been chosen as the incorporation element since Ti is a reactive metallic element with carbon. The effects of energetic $Ti^+$ ion implantation on the structures and tribological properties of DLC films deposited by unbalanced magnetron sputtering were investigated.

## 2. Experimental methods

The as-deposited DLC films of 100 nm were deposited on polished single-crystal silicon wafers (100) by unbal-

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anced magnetron sputtering of graphite target in a pure argon atmosphere at a pressure of 0.3 Pa for 1 h. Prior to deposition, the chamber was evacuated to a base pressure of $1\times10^{-3}$ Pa. The wafers Si (100) were ultrasonically cleaned in acetone and ethanol for about 10 min, respectively, placed into the $8\times10^{-1}$ Pa Ar environment, and cleaned with a 6-keV plasma for 10 min to remove surface contamination. The DC voltage of 450 V was applied to the target. A constant −100-V bias voltage was applied to the substrate. During deposition, the substrate was heated by a heater and the temperature was kept at 200 °C, measured by a thermocouple mounted behind the substrate.

Ti-doped DLC films were achieved by Ti ion implantation into the as-deposited DLC films in MEVVA80-10 ion implantation system. The implantation dose was $5\times10^{16}$ ions/cm$^2$ with an accelerating voltage of 30 kV.

The surface morphologies of the films were examined using Nanoscope IIIa atomic force microscopy (AFM) under ambient conditions. The root mean square (RMS) surface roughness was measured using the same device in contact mode.

The Raman measurements were carried out on a SPEX1430 Raman apparatus using the 488-nm line of an Ar ion laser focused to 50 μm. The laser power was 30 mW and the detecting range was from 1000 to 1800 cm$^{-1}$.

Transmission electron diffraction (TED) analyses were preformed using a JEM-100CXII microscope. The chemical states of the typical elements of the film were examined by X-ray photoelectron spectroscopy (XPS; PHI-5700 ESCA), operating with AlKα radiation at 250 W and a pass energy of 29.35 eV. The depth-profiling XPS analysis was performed with $Ar^+$ ion bombardment, at a beam voltage of 3 kV, beam density of 30 μm cm$^{-2}$, and sputter area of 4×4 mm$^2$. The sputtering time for each cycle is 2 min.

A UMT-2 pin-on-disk tribometer was employed to measure the friction coefficient of the DLC films at room temperature. Relative humidity in the measurement process was approximately 32%. A ball of 5 mm diameter made of GCr15 bearing steel ($w_t$ C 0.95–1.05%, Cr 1.30–1.65%, Si 0.15–0.35%, and Mn 0.20–0.40%) was pressed against the films with a normal load of 400 mN. The tests were conducted under a sliding velocity of 2 mm min$^{-1}$ and a sliding distance of 5 mm.

## 3. Results and discussion

### 3.1. Surface morphology

The surface morphologies of as-deposited DLC film and Ti-doped DLC film were shown in Fig. 1. Both the films show a smooth and uniform morphology. It is clear from this picture that the RMS surface roughness is

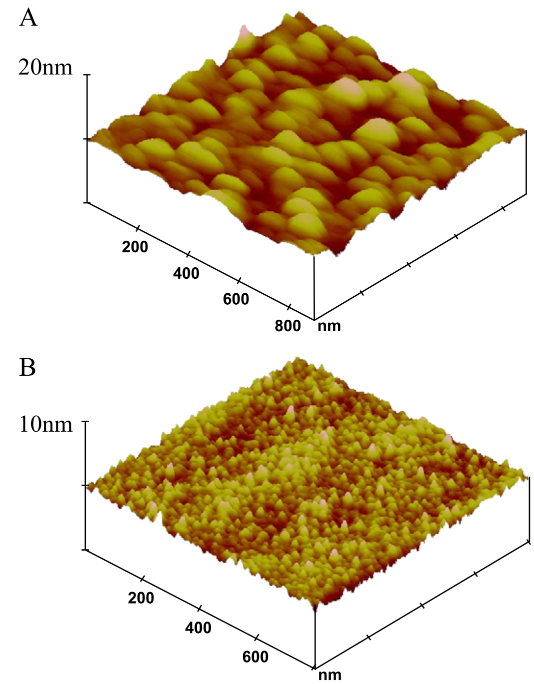


Fig. 1. AFM morphology of DLC films: (A) undoped and (B) doped.

reduced from 1.589 to 0.595 nm with $Ti^+$ implantation into the DLC film.

### 3.2. Raman spectroscopy

Raman spectroscopy is the best way to obtain the detailed bonding structures of DLC films. Fig. 2 shows the Raman spectra of as-deposited DLC film and Ti-doped DLC film. Both the Raman spectra exhibit a broad asymmetric peak in the range 1400–1700 cm$^{-1}$, which is typical of DLC films. This confirms that the films are amorphous. The figure also shows some obvious differences between as-deposited DLC film and Ti-doped DLC film. The Raman spectrum of Ti-doped DLC film has the obvious "shoulder" peak at 1350 cm$^{-1}$. It is presumably because of the increased contribution from the D-peak (disordered carbon) constituents in the film. The lower wavenumber "shoulder" peak means that the sp$^2$ content of Ti-doped DLC film increases for the $Ti^+$ implanted. In order to obtain quantitative information about the sp$^3$ content in the films, the experimental Raman spectra are considered as a combination of D (disorder) and G (graphite) peaks by Gaussian curves. G-peak around 1580–1600 cm$^{-1}$ and D-peak around 1350 cm$^{-1}$ are usually assigned to zone center phonons of $E_{2g}$ symmetry and $K$-point phonons of $A_{1g}$ symmetry, respectively, [6]. The sp$^3$ contents are calculated as the ratio between the area of G-peak and the area of D-peak ($I_D/I_G$). Wu and Hon [7] found the shift in the G-peak position to a lower frequency with decreasing of $I_D/I_G$, which means an increase in the fraction of sp$^3$ bonds. The position of G-peak shifts from 1560.7 to 1578.6 cm$^{-1}$ suggests the