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# Deposition of diamond-like carbon thin films containing photocatalytic titanium dioxide nanoparticles

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ABSTRACT

Diamond-like carbon (DLC) thin films containing photocatalytic titanium dioxide ($TiO_2$) nanoparticles were deposited by the plasma chemical vapor deposition method, which was developed by our group, using a colloidal solution as the precursor. It was found from the results of Raman spectroscopy, SEM observation and surface analyses that a bias voltage applied to the substrate had considerable effect on $TiO_2$ nanoparticle inclusion in the matrix DLC thin film, and the optimal bias voltage was in the range from −50 to −175 V. The depth profiling with Auger electron spectroscopy for the DLC thin film deposited at the bias voltage of −100 V suggested that $TiO_2$ nanoparticles were contained not only on the surface but also inside of the matrix thin film. To evaluate the photocatalytic properties of the deposited DLC thin films, methylene blue degradation, contact angle measurement, and antibacterial tests were performed. The results indicated that the DLC thin film containing $TiO_2$ nanoparticles exhibited the abilities to decompose methylene blue dye, make the surface more hydrophilic and kill *Escherichia coli* cells under ultraviolet light irradiation.



## 1. Introduction

Nanoparticle-dispersed composite films are expected to have the potential of changing their performances according to the individual properties of nanoparticles. Pioneering researches of the films having a structure of nanocrystal dispersion in the nitride matrix were performed by Veprek [1], who reported that the hardness of so-called nanocrystalline composites, nc-TiN/a-$Si_3N_4$ films exceeded 50 GPa, and in the case of nc-TiN/a-$SiN_x$ reached 105 GPa, corresponding to the hardness of diamond. Meanwhile, nanoparticle-dispersed thin films based on diamond-like carbon (DLC) matrix, having the features such as high hardness, wear resistance, low friction and biocompatibility, are attracting a great deal of attention in the field of tribological applications. TiC/DLC [2] and WC/DLC [3] systems were prepared using a hybrid process combining laser ablation and magnetron sputtering, and reactive magnetron sputtering, respectively, and were reported to exhibit higher tribological performance compared to pure DLC thin film.

For depositing nanoparticle-dispersed DLC thin films, our group developed a new plasma chemical vapor deposition (CVD) method using a colloidal solution of ready-made nanoparticles available as the precursor [4]. It is difficult to distribute the nanoparticles in a uniformly dispersed state in a matrix film because of their easy-to-aggregate properties. In this method the problem may be improved by the technique that the nanoparticles are carried into a CVD process chamber in a state of the aerosol. Using this method, silicon-containing DLC thin films were deposited with a colloid solution consisting of toluene, hexamethyldisilane and fullerene ($C_{60}$), and it was found that the thin films showed superior tribological property, lower friction [5].

On the other hand, titanium dioxide ($TiO_2$) is the leading material among lots of candidates for photocatalysts, and not only the superior decomposition and hydrophilic properties but also the highest stability are responsible for the industrial uses in the future [6]. The photocatalytic decomposition reaction can be utilized for antibacterial activity, and it is reported that *Escherichia coli* (*E. coli*) cells were killed by $TiO_2$ photocatalyst films prepared from titanium isopropoxide solution under ultra violet light irradiation [7]. F.R. Marciano et al. reported that DLC films containing $TiO_2$ nanoparticles were deposited by the plasma CVD and showed the antibacterial activity [8]. From the point of view of addition of bactericidal property to DLC thin film, elements such as fluorine [9] and silver [10] were incorporated into DLC.

In this study, on the purpose of preparing high durable photocatalytic antibacterial coating having both properties of DLC and $TiO_2$, DLC thin films were deposited using the developed plasma CVD system with a colloidal solution including $TiO_2$ nanoparticles as the precursor, and investigated for variation in the structural, compositional and photocatalytic properties against the deposition condition [11–13].

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## 2. Experimental

The developed plasma CVD system shown in Fig. 1 was used for depositing DLC thin films in this study [4,5]. The system consists of a CVD chamber equipped with an inductively coupled plasma (ICP) source and a nanoparticle-feeding device, and is characterized by using a solution containing nanoparticles in the colloidal state as the precursor. The nanoparticle-feeding device can make a colloid solution into the aerosol composed of the solvent vapor and uniformly dispersed nanoparticles by blowing an argon gas onto the nozzle in a vaporizer. The formed aerosol is carried into the chamber with the argon gas, and plasma CVD can be conducted.

A $TiO_2$ nanoparticle suspended toluene solution was prepared as the precursor for the DLC thin film deposition. The $TiO_2$ nanoparticles (ST-01, primary particle size: 7 nm, Ishihara Sangyo Kaisha, Ltd.) of 0.2 g and Aerosol-OT surfactant (sodium bis(2-ethylhexyl) sulphosuccinate) of 5 g were put into 100 ml toluene, and the solution was stirred with a magnetic stirrer for 2 h to be obtained as the milky-white suspended colloid. The colloid solution sent at a flow rate of about 30 mg/min was vaporized to be changed into the aerosol with argon carrier gas (flow rate: 40 sccm), and the aerosol was brought into the CVD chamber. ICP was generated by a 13.56 MHz radio frequency (RF) generator, and the power was set at 150 W. During deposition a bias voltage was applied to Si wafer used as the substrate by a 2 MHz RF generator, and varied in the range from −25 to −400 V. The substrate was water-cooled by the holder. The pressure was kept at 0.6 Pa during the deposition. The deposition time was 10 min, and before the deposition the substrate was cleaned by an argon plasma for 10 min.

The thicknesses of the deposited thin films were determined from profilometric measurements of a step formed during the deposition using a confocal laser microscope. Raman spectroscopy was carried out using an argon ion laser with a wavelength of 514.5 nm in the 300 to 1800 $cm^{-1}$ range. The surfaces of the deposited thin films were observed with a scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS) analysis was performed for each surface. The depth profiling analysis was conducted by means of measuring the spectra by Auger electron spectroscopy after argon ion etching of 30s to 150 min to the areas of 20×20 μm.

The following three kinds of tests were performed to evaluate the photocatalytic properties under ultraviolet (UV) light irradiation for the deposited DLC thin films. The first, positioned as the check test of presence or absence of photocatalytic property of all the deposited DLC thin films, methylene blue degradation tests were carried out to investigate the decomposition activity. The DLC thin film deposited Si substrates dipped in a $10^{-5}$ mol methylene blue solution (3.5 ml) were irradiated with UV light (wavelength: 352 nm, 20 W×2) up to 24 h, and the transmittances of the solutions were measured using an UV–vis spectrometer. The second, the wettability of the deposited DLC thin films under UV light irradiation was evaluated by contact angle measurement. A droplet of pure water was spotted on the surface of the DLC thin film after irradiation of UV light up to 180 min, and the contact angle was measured at the advancing edge of the water drop. Five separate measurements were performed on different locations, and the results represent an average of these measurements. Third, antibacterial tests were performed by the following procedure. The DLC thin film deposited Si substrates were placed in petri dishes, and 0.1 ml of *E. coli* (NBRC 3972) suspension in liquid culture medium was pipetted onto the surfaces of the DLC thin films. The substrates were under UV light (wavelength: 352 nm, 20 W×2) irradiation or in a darkroom for 3 h. After that, the cells were pipetted out from the substrates, and consecutive dilutions were prepared by taking the previous solution and mixing with purified water. Each solution of 1 ml was plated onto an agar medium. After incubating at a temperature of 37 °C for 18 h, the number of viable bacteria was counted.

In addition, to estimate the decomposition of DLC in itself by the photocatalytic effect, the deposited DLC thin films were irradiated with the UV light (wavelength: 352 nm, 20 W×2) up to 840 h (5 weeks), and investigated for the structural variation using Raman spectra measured in the range of 1000 to 1800 $cm^{-1}$.

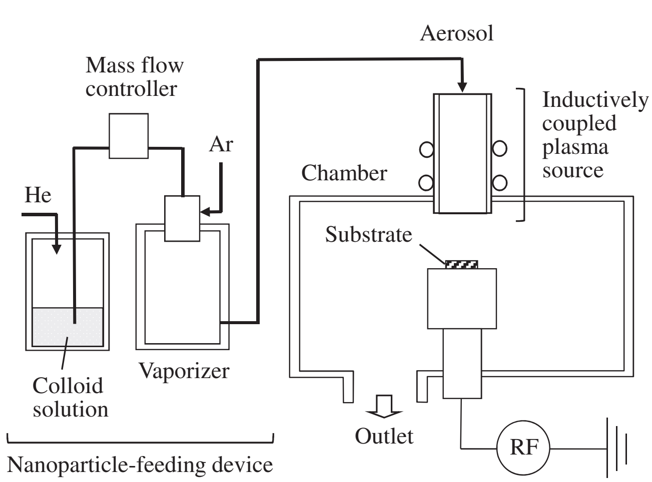


**Fig. 1.** Schematic diagram of the developed plasma CVD system.

## 3. Results and discussion

### 3.1. Structural and compositional properties

Fig. 2 shows the measurement results of the DLC thin film thickness as a function of the bias voltage. The thickness of the DLC thin films deposited monotonously increased from 0.76 to 1.3 μm with an increase in the bias voltage from −50 to −400 V. The deposition rate was found to be 76 to 130 nm/min, which was almost the same range as the previous result of DLC thin film deposition using aromatic hydrocarbon precursor [14].

The SEM observation results are shown in Fig. 3 for the surfaces of the DLC thin films deposited at the bias voltages of (a) −50, (b) −100, (c) −200 and (d) −400 V, respectively. The figure clearly indicates that a lot of particle-like projections with a few 100 nm to a few μm size can be dispersedly seen on the surfaces of (a) and (b), and few projections on (c) and (d). EDS analysis indicated that titanium was detected from the areas of the projections, suggesting that the projections were the aggregates of $TiO_2$ nanoparticles. From the point of view of wear resistance, the DLC thin films with the projections of $TiO_2$ aggregates, as shown in figures (a) and (b), unfortunately, are obviously guessed to be inferior to a conventional DLC thin film because of

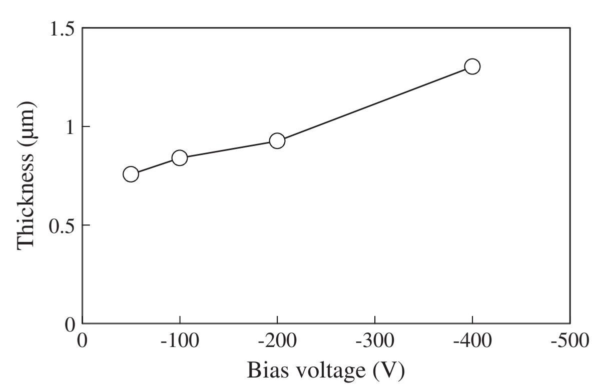


**Fig. 2.** The measurement results of DLC thin film thickness as a function of the bias voltage.