PHOTOCATALYTIC CHARACTERISTICS OF TITANIUM DIOXIDE CONTAINING DIAMOND-LIKE CARBON THIN FILM

Masahito Ban[1] *and Naoya Hasegawa*[2]

[1] Dept. of Systems Engineering, Nippon Institute of Technology, Saitama 345-8501, Japan
[2] Systems Engineering Major, Graduate School, Nippon Institute of Technology, Saitama 345-8501, Japan

Introduction

Nanoparticle-dispersed composite films are expected to have the potential of changing their performances according to the individual properties of nanoparticles. Diamond like carbon (DLC) thin films have the features such as high hardness, wear resistance, low friction and biocompatibility, and the film dispersed nanoparticles in the matrix is attracting a great deal of attention in the field of various applications. For depositing nanoparticle-dispersed DLC thin films, a new plasma chemical vapor deposition (CVD) method using a colloidal solution of ready-made nanoparticles available as the precursor has been developed. It is difficult to distribute the nanoparticles in a uniformly dispersed state in the 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 process chamber as the state of aerosol. Using this method, recently, the DLC thin films were deposited using a colloid solution consisting of both toluene solvent and fullerene (C_{60}), and it was found that the thin films showed superior tribological properties [1,2].

In this study, on the purpose of preparing high durable antibacterial coatings having both properties of DLC and titanium dioxide (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 the structural and photocatalytic properties [3,4].

Experimental

Depositions of DLC thin films were conducted by an inductively coupled plasma (ICP) CVD system equipped with a nanoparticle feeding device [1,2]. The ICP generation RF power was 150 W. During depositions bias voltages of -50 to -400 V were applied to Si substrates by an RF generator. The deposition pressure was kept at 0.6 Pa, and the deposition time was 10 min. As the precursor, a toluene solution suspended TiO_2 nanoparticles and surfactant was used.

For the structural and componential evaluation, raman spectroscopy and energy dispersive x-ray spectroscopy (EDS) analysis were performed.

As the evaluation of the photocatalytic properties under ultraviolet light irradiation, methylene blue degradation tests were carried out. Ultraviolet light (wavelength: 352 nm, 20 W ×2) was irradiated the DLC thin film deposited substrate dipped in a 10^{-5} mol methylene blue solution (3.5 ml) up to 24 h, and the transmittances were measured using an UV-Vis spectrometer. Also, antibacterial tests were performed by the following procedure. The DLC thin film deposited substrates were placed in petri dishes, and 0.1 ml of Escherichia coli (NBRC 3972) suspension in liquid culture medium was pipetted onto the surface of the deposited films. The substrates were under ultraviolet 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. From each solution 1 ml was plated onto an agar medium. After incubating at a temperature of 37 ℃ for 18 h, the number of viable bacteria was counted.

Results and Discussion

Fig. 1 shows the EDS analysis results for the DLC thin films deposited at bias voltages of -50 to 400 V. From the figure, the peaks of titanium and oxygen were confirmed for the DLC thin films with the bias voltages of -50 V and -100 V. The raman spectrum of the DLC thin film deposited at a bias voltage of -100 V is shown in Fig. 2. Concerning the thin film,

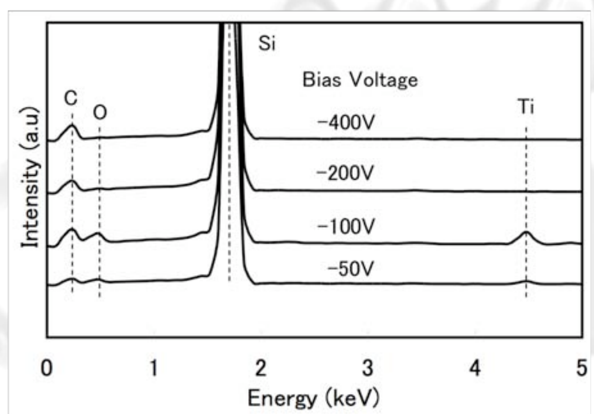

Fig. 1 The EDS analysis results for the DLC thin films deposited at the bias voltages of -50 to -400 V.

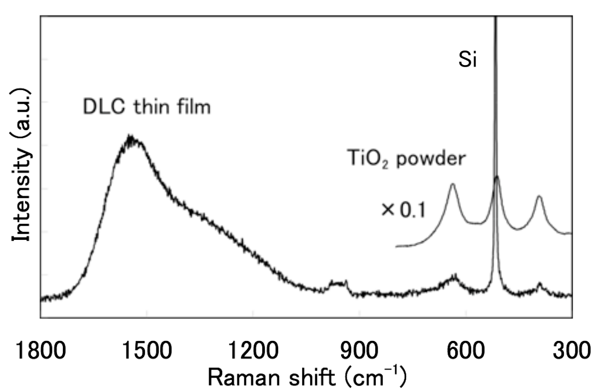

Fig. 2 The raman spectra for the DLC thin film deposited at bias voltage of -100 V and TiO_2 powder.

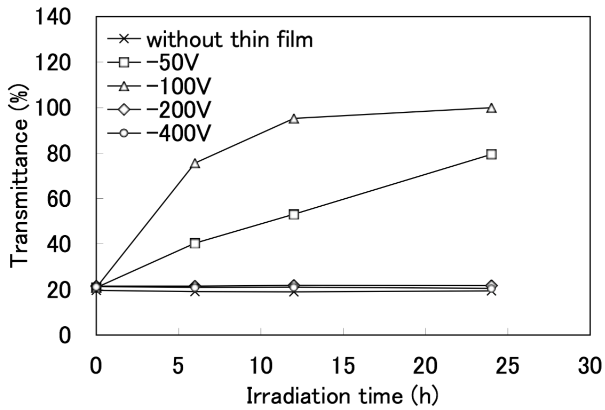

Fig. 3 The measurement results of transmittances as for the DLC thin films deposited with bias voltages of -50 V to -400 V as a function of ultraviolet light irradiation time.

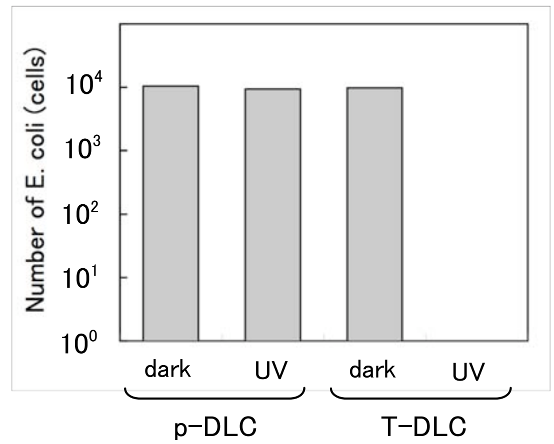

Fig. 4 The antibacterial test results: the number of viable E. coli after 3 h staying in a darkroom (dark) and ultraviolet light irradiation (UV) of 3 h.

the peaks (400 cm^{-1} and 640 cm^{-1}) attributed to TiO_2 were detected in addition to both G-peak (1570 cm^{-1}) and D-peak (1350 cm^{-1}) generally observed from the structure of typical DLC thin film. It was suggested from these results that the DLC thin films at the bias voltages of -50 V and -100 V contained TiO_2 nanoparticles. The inclusion of TiO_2 nanoparticles may occur due to the incorporation into the DLC thin film during the deposition process of decomposition products of toluene as DLC matrix on the substrate. In the case, it is highly probable that the optimal bias voltage exists for the nanoparticle inclusion depending on the charging state of the nanoparticles suspended in the plasma.

The transmittances measured by the spectrometer are shown as a function of the irradiation time of ultraviolet light as the results of the methylene blue degradation tests using the DLC thin films deposited under the bias voltages of -50 to -400 V. The measurement result in the case performed without the DLC thin film is added in the figure. It was found that the transmittance for the DLC thin film at the bias voltage of -100 V drastically increased with an increase in the irradiation time to be about 100 % in 12 h. Also, the DLC thin film at the bias voltage of -50 V showed about 80 % of transmittance at 24 h of the irradiation time. On the contrary, in the case of the DLC thin films deposited at -200 V and -400 V, the transmittance showed little variation and kept the initial value; about 20 %. The results demonstrated that the DLC thin films deposited with the bias voltages of -50 V and -100 V had the ability to decompose methylene blue dye under ultraviolet light irradiation.

Fig. 4 shows the number of viable E. coli after 3 h staying in a darkroom (dark) and ultraviolet light irradiation (UV) of 3 h as the antibacterial test results for the DLC thin film deposited at the bias voltage of -100 V (T-DLC) and pure DLC thin film deposited from only toluene (p-DLC). It was clearly indicated that the number of E. coli became nearly zero only in the case that T-DLC was irradiated ultraviolet light. Meanwhile, the number of E. coli for p-DLC was on the order of 10^4 cells even under ultraviolet light irradiation. Therefore, the test results demonstrated that E. coli cells were completely depressed due to ultraviolet light irradiation to T-DLC, and implied that the DLC thin film deposited at -100 V exhibited the antibacterial activity by the photocatalytic ability.

Summarizing the above results, it is suggested that the DLC thin films deposited with the bias voltages of -50 V and -100 V embedded TiO_2 nanoparticles not only in the matrix film but also on the film surface, resulting in showing the photocatalytic ability.

Conclusions

The results of EDS and raman analysis implied that the DLC thin films obtained under the specific deposition conditions, the bias voltages of -50 and -100 V, included TiO_2 nanoparticles in the matrix. The methylene blue degradation and the antibacterial tests were conducted under ultraviolet light irradiation, and it was found that the TiO_2 containing DLC thin films showed the effective photocatalytic activity.

References

[1] S. Shimizu, M. Ban, H. Okado, T. Suemitsu. Development of nanoparticle dispersive diamond-like carbon film. Proceedings of International Tribology Conference. 2005;Kobe:379.

[2] H. Shimizu, M. Ban. Preparation and tribological properties of nanoparticles containing diamond-like carbon films. World Tribology Congress 2009 Proceedings. 2009;Kyoto:446.

[3] M. Ban, N. Hasegawa, T. Sato, M. Suzuki. Deposition of diamond-like carbon films containing titanium dioxide. 19th European Conference on Diamond, Diamond-Like Materials, Carbon Nanotubes and Nitrides Proceeding. 2008;Sitges:P1.6.7.

[4] M. Ban, T. Amamiya, N. Hasegawa. Preparation and properties of diamond-like carbon films containing photocatalytic titanium dioxide. Carbon 2009 Presentation Extended Abstracts. 2009;Biarritz:440.