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（様式第５号）

同軸型アークプラズマ成膜法で作製したナノダイヤモンド薄膜の化学結合状態が上皮細胞の付着に与える影響と歯科インプラントへの応用

Effects of Chemical Bonding Structure of Nanodiamond Thin Films Deposited by Coaxial Arc Plasma Deposition on Adhesion of Epithelial Cells and Application to Dental Implants

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１．概要（注：結論を含めて下さい）

This study focused on the fabrication of hard nanodiamond composite films (NDC)on titanium (Ti) substrates under negative bias voltages using hybrid coaxial arc plasma deposition (CAPD). The deposition process was carried out with varying substrate bias voltages and a pure graphite target, without any inserted gases, at a pressure of 10^{-5} Pa. The effects of the substrate bias voltage on the deposition process, as well as the mechanical and structural properties of the films, were investigated. It was found that at an optimal bias voltage of -40 V, accelerated positive carbon ions facilitated favorable deposition conditions for nanocrystalline diamond growth, resulting in hard films with superhardness of 96 GPa which is close to diamond gem. The study also employed X-ray photoelectron and near edge X-ray absorption fine structure spectroscopies to confirm the enhancement of sp^3-C hybridization carbon in the deposited films with 89%, which was consistent with the improved mechanical properties due to enhanced C 1s (σ*) transitions. The adhesion, growth, differentiation and osseointegration of epithelial cells are expected to be significantly improved in dental implants due to the highly biocompatible diamond content (89%) proposed by these films. The improved cell adhesion is caused by the organic layer adsorbed on the films from the cell medium. The adsorbed layer has greater adhesion to NDC films' surface due to strong diamond surface dipoles that could be generated by further hydrogen or oxygen surface termination. Therefore, the NDC coatings supported epithelial cells better than the reference Ti substrate.

２．背景と目的

Nanodiamond composite (NDC) films nowadays have grabbed global researchers' attention. Comprising diamond crystallites (less than10 nm in diameter) within an amorphous carbon vicinity imparts in them merit properties. Synergistic mechanical, tribological, and biocompatible features of NDC films are thought provoking for implants and artificial joints. Fundamentally, NDC films have superior biocompatibility as one of the most practical carbon allotropes which is the principal constituent of a living organism.

Jointly, pure titanium (Ti) is the broadly utilized implant candidate because of its exceptional lightness, strength, corrosion resistance, and biocompatibility However, Ti partially endures bio-tribocorrosion upon biological enclosure, causing Ti debris ejection into surrounding tissues, and their systemic dissemination and precipitation in distant organs. Mutual implant–organism reactivity leads to aseptic loosening (bone resorption and poor osseointegration) and bacterial infection. As a consequence, patients bear pain, allergic reactions, and inflammation resulting in implant failure and costly revision surgeries. One promising solution, is protective diamond film implementation to Ti implants for their bio-tribocorrosion and osseointegration enhancement.

In our pervious study, we acquired impressing mechanical and structural properties of the NDC films on Ti via a hybrid system of ion etching gun and coaxial arc plasma deposition (IG/CAPD) at room temperature. Motivated by the results, in this study we implement the application of negative bias voltages during the growth of NDC films on Ti. The influence of the applied variable bias voltage was further investigated in terms of mechanical and structural characterization. The application of the negative bias voltages during the growth of NDC films is expected to reinforce the sp3-fraction of the films by selective etching of sp^2-C bonded atoms by the highly energetic C+ ions accelerated from the plasma towards the Ti substrates where they are quenched into sp^3-C bonded atoms. The higher content of diamond in the films is expected to improve the adhesion strength of epithelial cells to the UNCD films due to their excellent biocompatibility and strong surface energy. The surface energy can be modified by terminating the surface with oxygen, nitrogen, or fluorine, which could facilitate the growth and differentiation of stem cells into various human body cells. In vitro investigation of the improved mechanical and structural NDC films are under investigation jointly with Kyushu University Hospital.

３．実験内容（試料、実験方法、解析方法の説明）

In this study, NDC films were deposited on negatively biased Ti substrates using the hybrid IG/CAPD system with a graphite target at base pressures less of 10^{-5} Pa. The film deposition was carried out on Ti substrates with dimensions of 10×10 mm. Different bias voltages were applied to the substrate holder from 0V to -100 V during deposition with the arc plasma gun, that is equipped with a 720 μF capacitor, and with a discharge repetition rate of 1 Hz. The films' hardness and Young's modulus were evaluated by nanoindentation with an applied indentation load of 0.5 mN/10 s, while the adhesion strength was assessed by a scratch test. The chemical bonding structures of the films were characterized using X-ray photoelectron and near edge X-ray absorption fine structure (NEXAFS) spectroscopies.

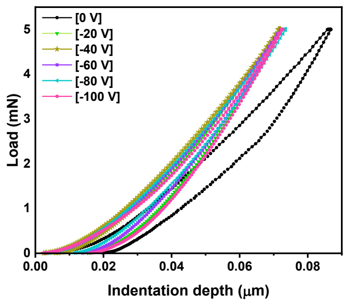

Fig.1. Load-displacement curves of NDC films on Ti.

4．実験結果と考察

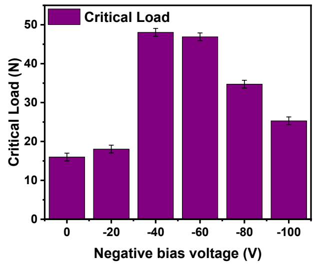

Fig.2. Adhesion strength of NDC films on Ti.

The nanoindentation load-displacement curves, as illustrated in Fig.1, were utilized to evaluate the hardness of the fabricated films. The results showed that increasing the bias voltage led to a corresponding increase in both hardness and Young's modulus. At a bias voltage of -40 V, the hardness was drastically improved to be 96 GPa which is comparable to diamond gem. The negative bias voltage of the substrate played a crucial role in enhancing the mechanical properties of the films, especially the hardness. This was attributed to the electrical attraction of positively charged carbon species to the negatively biased substrates. The scratch test was employed to evaluate the adhesion strength of the UNCD/a-C films, as depicted in Figure 2. The critical loads of the NDC films fabricated at different bias voltages indicated a remarkable improvement in the adhesion strength with increasing negative bias voltage. The critical load of the films fabricated for the unbiased film was found to be 16 N, which increased significantly to 48 N when fabricated at the optimal bias voltages of -40 V. This is attributed to a formation of a TiC interfacial layer due to highly energetic C^+ ions that is sub-implanted underneath Ti substrate's surface.

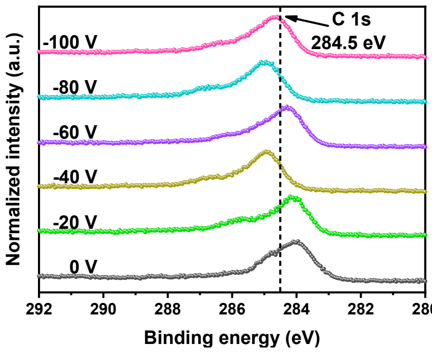

Fig.3. C 1s photoemission spectra of NDC films on Ti.

For a complementary structural analysis, C 1s photoemission spectroscopy has been conducted for NDC films at different bias voltages. At lower bias voltages, the spectra tend to slightly shift to lower binding energies with respect to C 1s peak at 285.5 eV which may result in more sp^2-C bonded atoms in the films. At the optimal bias voltage of -40V, the spectra have the highest tendency to shift towards the higher binding energies which indicates more sp^3-C fraction in the films of 89% calculated by deconvolution of C 1s photoemission spectra into component peaks using Voigt function. Theses results are consistent with the superhardness of the films of 96 GPa at the optimal bias voltage of -40V.

5．今後の課題

In this study we obtained novel superhardness of the NDC films at an optimal bias voltage of -40V. The significant increase in the hardness of the films at this optimal bias voltage is correlated to increased sp^3-C fraction in the films which is synergistically enhanced by the sub-implantation of the highly energetic C^+ ions underneath Ti substrate's surface. These remarkable results are expected to promote interesting adhesion and osseointegration of the epithelial cells due to the highly biocompatible diamond content in the films (89%) for the application in dental implants. In vitro investigation of the optimal NDC films are currently progressed with cooperation with Kyushu University Hospital..

6．参考文献

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7．論文発表・特許（注：本課題に関連するこれまでの代表的な成果）

該当なし

8．キーワード（注：試料及び実験方法を特定する用語を２～３）

Nanodiamond composite films, Negative bias growth, Titanium, Coaxial arc plasma deposition

９．研究成果公開について（注：※２に記載した研究成果の公開について①と②のうち該当しない方を消してください。また、論文（査読付）発表と研究センターへの報告、または研究成果公報への原稿提出時期を記入してください。提出期限は利用年度終了後 2 年以内です。例えば 2018 年度実施課題であれば、2020 年度末（2021 年 3 月 31 日）となります。）
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① 論文（査読付）発表の報告 **（報告時期：2025 年 3 月）**