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（様式第５号）

基板への負バイアス印加が超ナノ微結晶ナノダイヤモンド膜の化学結合状態に与える影響

Effects of negative bias applied to substrates on the chemical bonding structures of ultrananocrystalline diamond films Soft

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※１　先端創生利用（長期タイプ）課題は、実施課題名の末尾に期を表す（Ｉ）、（Ⅱ）、（Ⅲ）を追記してください。
※２　利用情報の公開が必要な課題は、本利用報告書とは別に利用年度終了後２年以内に研究成果公開｛論文（査読付）の発表又は研究センターの研究成果公報で公表｝が必要です (トライアル利用を除く)。
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１．概要（注：結論を含めて下さい）

Ultrananocrystalline diamond (UNCD)/amorphous carbon (a-C) composite (UNCD/a-C) films were deposited on WC-Co substrates, which were pulsed-biased at a voltage of −100 V and frequencies from 40 to 80 kHz, by coaxial arc plasma deposition. The bias effects on the mechanical and structural properties of the UNCD/a-C films were investigated. The deposition rate increased approximately threefold by applying the bias, which implies that species ejected from a coaxial arc plasma gun are ionized. A 9 µm UNCD/a-C film with a hardness of 49 GPa was deposited at a low frequency of 40 KHz. With increasing pulse bias frequency, the hardness was degraded. X-ray photoelectron and near-edge X-ray absorption fine-structure spectroscopic measurements indicated that the amount of sp^3 bonds is evidently decreased due to the undesirable surface charge up. It worked on reducing the negative bias voltage and ion energy at the high bias frequency.

２．背景と目的

Ultrananocrystalline diamond (UNCD)/nonhydrogenated amorphous carbon (a-C) composite (UNCD/a-C) films are new candidates applicable to hard coating because of the high hardness and extremely smooth film surface.[1] It is well known that the physical properties of carbon materials are strongly influenced by the ratio of sp^3 (diamond-like) to sp^2 (graphite-like) bonds. The mechanical properties of UNCD/a-C films, which comprise a large number of UNCD grains and an a-C matrix, are expected to be strongly affected by the ratio between sp^3 and sp^2 bonds.

In our previous studies, we realized the formation of 51-GPa-hardness UNCD/a-C films on cemented carbide (WC-Co) substrates by coaxial arc plasma deposition (CAPD), without applying negative bias to substrates. They exhibited the $sp^3/(sp^3+sp^2)$ ratio of 57%, which was estimated from X-ray photoemission measurements. To enhance the mechanical properties of UNCD/a-C films, the negative bias voltage was applied to substrates during the deposition. Since the application of the negative bias onto substrates enhances the kinetic energies of ionized species, an improvement in the mechanical properties of resultant films is expected.

According to a grain boundary mismatch model (GBM) and an ion-peening model (Ion-P.),[6] which describe the residual stress as a function of the ion energy,[7] with increasing the ion energy the internal stress of the films gradually decreased. Therefore, the ratio of sp^3 bonds is expected to increase by applying the negative bias due to increasing the energy of deposited carbon ions and reducing the internal stress of the films. In this work, the effects of negative bias on the deposition of UNCD/a-C films on WC-Co substrates was studied, and the chemical bonding structures of the films were investigated by X-ray photoelectron and near-edge X-ray absorption fine-structure spectroscopies.

３．実験内容（試料、実験方法、解析方法の説明）

UNCD/ a-C films were deposited on negatively-biased WC-Co substrates at base pressures of less than 10^{-4} Pa by CAPD. The substrates were pulsed-biased at a negative voltage of –100 V and frequencies of 40, 60, and 80 kHz. The hardness and Young's modulus of the UNCD/a-C films were estimated by nanoindentation at an applied indentation load of 0.5 mN. The film thickness was evaluated from cross-sectional SEM images. X-ray photoelectron and near-edge X-ray absorption fine structure (NEXAFS) spectroscopies were employed for characterizing the chemical bonding structures of the films at beamline 12 of Kyushu Synchrotron Center/Saga Light Source.

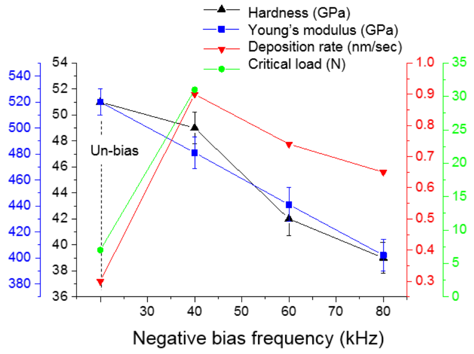

Fig. 1. Dependence of hardness, Young's modulus, deposition rate, and critical load on bias frequency.

４．実験結果と考察

It was found that the application of negative bias trembles the deposition rate, as compared with that of the films deposited without biasing. The critical load estimated from scratch tests was improved by four times by biasing.

The hardness and Young's modulus were hardly affected by the bias frequency, as show in Fig. 1. The hardness was 49 GPa and the fraction of sp^3 was 57% at a bias frequency of 40 kHz. Figure 2 shows X-ray photoemission spectra of the films deposited at bias frequencies of 40 and 80 kHz. The hardness and sp^3 fraction decreased with increasing bias frequency.

NEXAFS measurements were examined to study the chemical bonding structures of the films. Figure 3 shows typical NEXAFS spectra of the films deposited at zero bias and different bias frequency of 40 and 80 kHz. The intensity of spectra was normalized at 330 eV and the background was subtracted by using the Victorian –fit method. The spectra show a sharp rise near 284.5 eV (π* C=C), which may be raised from amorphous carbon matrixes in UNCD/a-C films. On the other hand, there is a separated peak at 295 eV and a slightly deep valley near 300 eV related to (σ* C-C) in UNCD/a-C film deposited at zero bias condition. These separated peaks and deep valley disappears for the films deposited at bias frequency of 40 and 80 kHz.

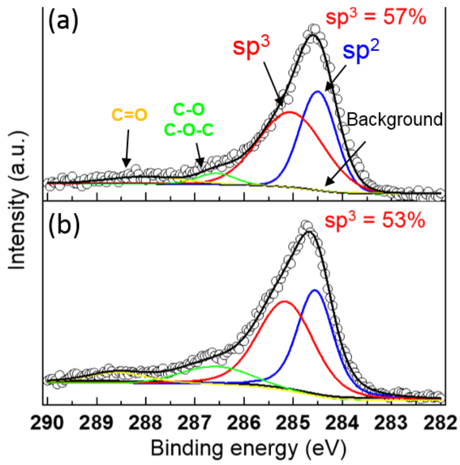

Fig. 2. Typical C 1s X-ray photoelectron spectra of films deposited at bias frequency of (a) 40 kHz and (b) 80 kHz.

５．今後の課題

In this work, we could confirm the decreased sp^3 content responsible for the regarded hardness and Young's modules of the negatively biased films. The surface charge up phenomena was observed during the films deposition, and it worked on reducing the negative bias voltage and ion energy at the high bias frequency. Therefore, the surface charge up produce more graphitic carbon bonds and reduce the hardness. The results point out that changing the pulsed bias parameters do affect UNCD/a-C film properties. Therefore, we expect that the properties of UNCD/a-C films can be controlled and improved by selecting suitable bias conditions.

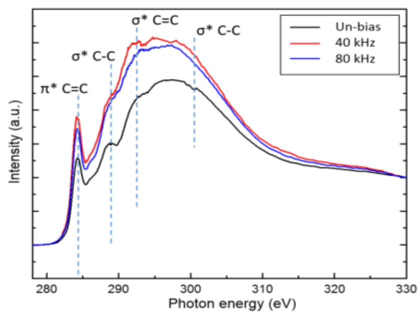

Fig. 3. Typical NEXAFS profile of UNCD/a-C films deposited on WC-Co at deferent substrate bias conditions.

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）

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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, Negative bias voltage, Hard coating, 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（2018 年度実施課題は 2020 年度末が期限となります)。
長期タイプ課題は、ご利用の最終期の利用報告書にご記入ください。

① 論文（査読付）発表の報告　　　　（報告時期：2020 年 12 月）