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（様式第４号）

同軸型アークプラズマ成膜法における負バイアスおよび窒素ドーピングが超硬基板上に成膜した超ナノ微結晶ダイヤモンド/アモルファスカーボン混相膜の化学結合状態に与える効果

Effects of Negative Bias and Nitrogen-doping on Chemical Bonding Structure of Ultrananocrystalline Diamond/Amorphous Carbon Films Deposited on WC-Co Substrates by Coaxial Arc Plasma Deposition

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１．概要（注：結論を含めて下さい）

Hard nanodiamond composite films were fabricated on negatively biased tungsten carbide substrates by coaxial arc plasma deposition. The deposition was performed at different substrate bias voltage using a pure graphite target of arc gun at a pressure less than 10^{-4} Pa without inserted gases. The influences of the substrate bias voltage on the deposition process, mechanical and structural properties of the films were investigated. At appropriated bias voltage, the accelerated positive carbon ions have shown prudent deposition condition favorable for nanocrystalline diamond growth. As a result, hard films of 80 GPa were performed at a bias voltage of -120 V. The outcomes of X-ray photoelectron and near-edge X-ray absorption fine structure spectroscopies certified the enhancement of sp^3 hybridization carbon. This significant improvement in the mechanical properties is consistent with enhanced C 1s→ σ* transitions in the deposited films.

２．背景と目的

Ultrananocrystalline diamond/ amorphous carbon (UNCD/a-C) coating, a suitable mechanical form of carbon nanomaterials with a composite structure of amorphous carbon (sp^2 and sp^3 hybridization) and nanodiamond crystallites, have excellent hardness, chemical inertness, biocompatibility, wear-resistance and surface smoothness as well as low friction coefficient. Chemical vapor deposition (CVD) has been essentially employed for nanodiamond films deposition. Recently, pulsed coaxial arc plasma deposition (CAPD) has been used as a typical physical vapor deposition (PVD) method with significantly improved properties over the CVD growth techniques.

To improve the deposition ability of the CAPD system and increase the energy of the deposited plasma species, the development of coating systems was driven by negatively biasing the substrate during the deposition. This work was primarily aimed to study the influence of different negative bias voltage on the growth of UNCD/a-C films prepared by CAPD. The effects on the mechanical and structural properties of the films were investigated.

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 with a graphite target. WC–Co substrates (K-type cemented tungsten carbide) with a dimension of 10×4.5 mm were employed for film deposition. A voltage of 100 V was applied to the arc plasma gun equipped with a 720-µF capacitor. The repetition rate of discharges was 1 Hz. The substrate holder was biased at a voltage of -40, -60, -80, -120 V.

The hardness and Young's modulus of the films were estimated by nanoindentation with an applied indentation load of 0.5 mN/10 s. The adhesion strength of the fabricated films was evaluated by a scratch test. X-ray

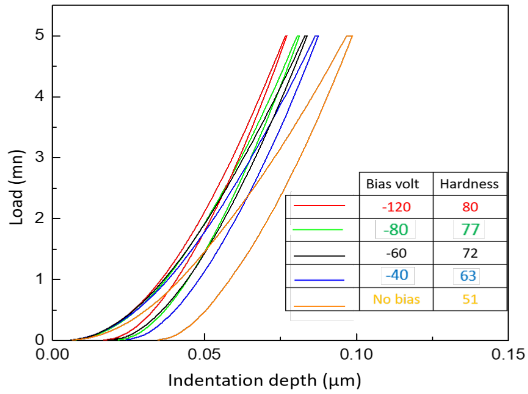

Figure 1 Load–displacement curve of UNCD/a-C films deposited at negative bias voltage of -120 (red), -80 (blue), -60 (black), -40 Volts (green), and no bias voltage (yellow).

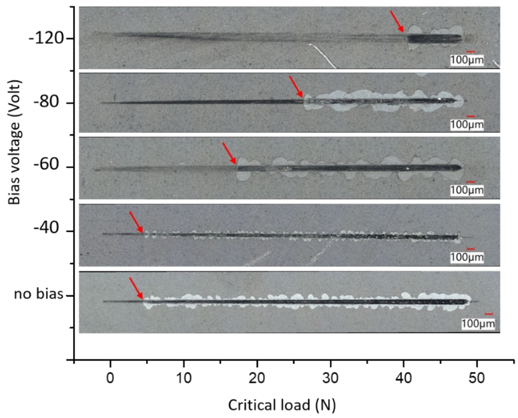

Figure 2 Adhesion strength measured by scratch testing of UNCD/a-C films deposited at different bias voltage

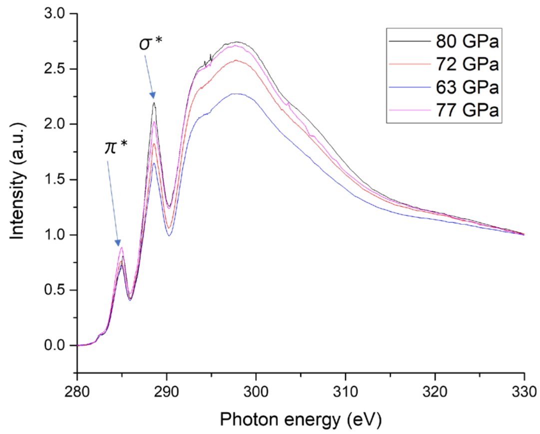

Figure 3 NEXAFS spectra of UNCD/a-C films with different hardness.

photoelectron and near-edge X-ray absorption fine structure (NEXAFS) spectroscopies were employed for characterizing the chemical bonding structures of the films.

４．実験結果と考察

The hardness of the fabricated films were evaluated from the load-displacement curves obtained from nanoindentation as shown in Fig. 1. It clearly shows that the hardness and Young's modulus increases with increasing the bias voltage. The hardness at -120 V was 80 GPa. The substrate with a negative bias voltage has a major role in enhancing the mechanical properties, including hardness, which indicates that the negative bias electrically attracts positively-charged carbon species to the substrates. The adhesion strength measured by scratch testing of UNCD/a-C films has shown marked improvement with increasing the negative bias voltage, as shown in Fig. 2. The presented Figure shows a micrograph of the scratch tested UNCD/a-C films fabricated at different bias voltage. The critical load of the films fabricated without bias voltage was found to be 7 N which rose to 19 and 28 N when fabricated at bias voltage of -60 and -80 V, respectively. The top image presents how the film fabricated at -120 V was able to withstand a scratching load up to 40 N. For a complementary structural analysis, NEXAFS spectroscopy was obtained for the deposited samples. Figure 3 shows NEXAF spectra exhibit sharp absorption bands from a C 1s→ σ* and C 1s→ π* transitions, which are characteristic of sp^2 and sp^3 hybridized carbon (double bond) and (single bond), respectively. The relative intensity of σ* peak gradually enhanced compared with the π* peak, with the bias voltage, which agrees with hardness enhancement. This might imply that the negative bias plays a role in enhancing the formation of nanocrystalline diamond and reducing the internal stress of the films.

５．今後の課題

In this work, the role of negative bias in the enhancement of mechanical properties, and the relationship between the film hardness and C 1s→ σ* and C 1s→ π* transitions were investigated. The results demonstrated that the use of negative bias enhance the formation of sp^3 bonds which work on improving the mechanical properties of the deposited films.

６．参考文献

[1] A. M. Ali *et al.*, *Diam. Relat. Mat.* **96**, 67 (2019).
[2] Y. S. Li *et al.*, *J. Appl. Phys.* **101**, 073503 (2007).
[3] A. M. Ali *et al.*, *Appl. Phys. Express* **13**, 065506 (2020).
[4] A. M. Ali *et al.*, *Surf. Coat. Technol.* **417**, 127185 (2021).

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, Coaxial arc plasma, negative bias, Hardness, near-edge X-ray absorption fine structure.

９．研究成果公開について

① 論文（査読付）発表の報告　　　　（**報告時期：2021 年 3 月**）