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（様式第４号）

同軸型アークプラズマ堆積法によりバイアス印加下で堆積されたナノダイヤモンド膜の化学結合構造

Chemical bonding structures of nanodiamond films deposited under negative biases by coaxial arc plasma deposition

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※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）

Nanodiamond composite (NDC) films, wherein diamond nanocrystallites with diameters of less than 10 nm are embedded in an amorphous carbon (a-C) matrix, have received much attention since they possess physical properties similar to those of diamond and relatively smooth surfaces. They are promising candidates for a variety of applications such as electronic devices, detectors, hard coating, microelectromechanical systems (MEMS), and nanoelectromechanical system (NEMS). NDC films were deposited by coaxial arc plasma deposition (CAPD) on cemented carbide (WC-Co) substrates with negative bias voltage during the deposition. The films deposited on a biased substrate achieved an evident enhancement in the hardness to 60 GPa and Young’s modulus to 635 GPa, as compared with the hardness of 50 GPa and Young’s modulus of 520 GPa of films deposited without negative bias. This significant improvement in the mechanical properties is consistent with enhanced C 1s→ σ* transitions in the films.

２．背景と目的

Nanodiamond composite (NDC), comprising nanodiamond grains of less than 10 nm in diameter and an a-C matrix, is a carbon-based nanomaterial applicable to hard and biomedical coatings, due to high hardnesses, low friction coefficients, and high affinities for living bodies. Nano-composite structures have received much attention, since enhancements in the hardness, friction and wear performance are expected due to the nano-composite structures. At present, the research has meanly focused on the preparation of nanodiamond films by chemical vapor deposition (CVD), microwave plasma and hot filament assisted chemical vapor deposition. But there has been less research on the effects of negative bias voltage on the deposition and properties of the nanodiamond films. It is well known that negative bias application to substrates enhances their mechanical properties, particularly the hardness and adhesion strength, of DLC films prepared by physical vapor deposition. This work was primarily aimed to study the influence of different negative bias frequency on the growth of NDC films prepared by coaxial arc plasma deposition (CAPD). The effects on the mechanical and structural properties of the films were investigated.

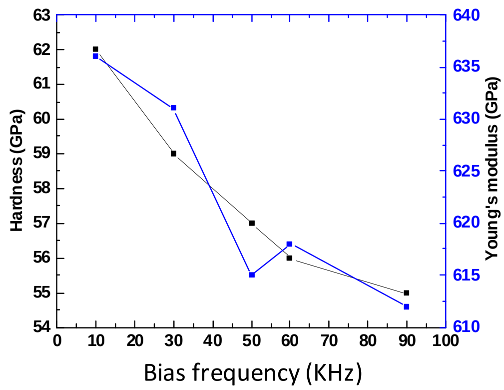

Figure 1 Dependence of hardness and Young's modulus on negative bias frequency.

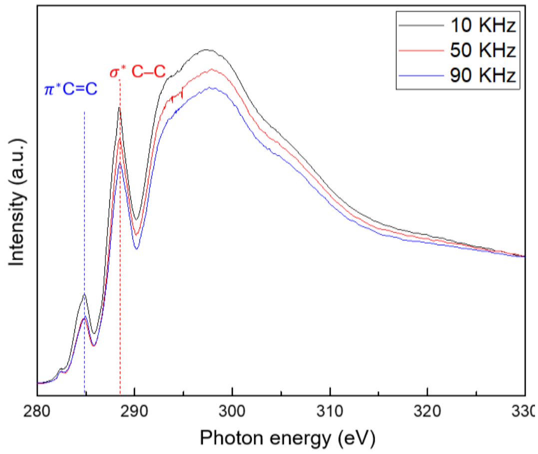

Figure 2 NEXAFS spectra of NDC films deposited at negative bias frequency of 10 KHz (black), 50 KHz (red), and 90 KHz (blue).

３．実験内容（試料、実験方法、解析方法の説明）

NDC 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 –80 V in pulse with a frequency of 10, 30, 50, 70 and 90 kHz. The hardness and Young's modulus of the films were estimated by nanoindentation with an applied indentation load of 0.5 mN/10 s. X-ray 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 negative bias frequency dependence of the hardness (black line) and Young's modulus (blue line) are shown in Fig. 1. It clearly shows that the hardness and Young's modulus increases with decreasing bias frequency. The hardness and Young's modulus at 10 kHz are 62 GPa and 636 GPa, respectively. The negative bias application increased the hardness by 10 GPa as compared with that of the films deposited under no bias, which indicates that the negative bias electrically attracts positively-charged carbon species to the substrates. For a complementary structural analysis, near-edge X-ray absorption fine structure (NEXAFS) spectroscopy was obtained for the deposed samples (see fig. 2). The spectra exhibit sharp absorption bands from a C 1s→ σ* and C 1s→ π* transitions, which are characteristic of sp^2 and sp^3hybridized carbon (double bond) and (single bond), respectively. The relative intensity of σ* peak gradually enhanced compared with the π* peak, with decreasing the negative bias frequency, which agrees with hardness enhancement by decreased bias frequency. 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 films 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 sp3 bonds which work on improving the mechanical properties of the deposited films.

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, 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）