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（様式第５号）

タングステンバッファ層を有する超硬合金基板及び Si 基板上に堆積したナノダイヤモンドコンポジット膜の機械特性と化学結合構造との相関の解明（Ⅱ）

Study on relationship between mechanical properties and chemical bonding structures of nanodiamond composite films deposited on cemented carbide with tungsten buffer layer and Si substrates (II)

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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, which comprise nano-diamond crystals embedded in amorphous carbon matrix (a-C) can be applied in a variety of fields owing to their superior electrical, optical, and mechanical properties. The high hardness and extremely smooth surfaces of NDC films as compared with those of polycrystalline diamond films are keys for the application to hard coating on cemented carbide and silicon substrates, which are representative substrates for cutting tools and electronic devices, respectively. NDC films were deposited by coaxial arc plasma deposition (CAPD) on cemented carbide (WC-Co) substrates directly and with tungsten (W) intermediate layers.

The films deposited on W intermediate layers achieved an evident enhancement in the hardness to 67.5 GPa and Young’s modulus to 719 GPa, as compared with the hardness of 50 GPa and Young’s modulus of 520 GPa of films deposited directly on the substrates. This significant improvement in the mechanical properties is consistent with enhanced C-C sp^3 fractions in the films. It was found that the W intermediate layers suppress Co catalytic effects that induces graphitization specially at the interface and thus improve formation of diamond crystals and enhances films adhesion.

２．背景と目的

Diamond and related hard carbon coatings have attracted attention because they are effectively applicable to cutting non-ferrous and abrasive materials due to their unique features such as high hardness and excellent mold release. The physical properties of carbon materials are strongly influenced by the ratio of sp^3 (diamond-like) to sp^2 (graphite-like) bonds. Nanodiamond composite (NDC) films deposited directly on WC-Co at room substrate-temperature exhibit maximum hardness of 50 GPa and a young's modulus of 520 GPa [1]. It was demonstrated that low substrate temperature is effective to diamond growth and suppressing the Co catalytic effects at the interface. Furthermore, the diffusion of Co atoms into the films hardly occurs even at the substrate temperature of 550 ºC. To further understand the role of Co catalytic effects on the properties of the films, W intermediate layer was sputtered prior to the film deposition, because it was reported that the insertion of W intermediate layer can improve diamond growth rate with finer grain structure, achieve highest nucleation density of diamond comparing to other strong carbide-forming elements (Ti and Cr), and suppress Co catalytic effects and compressive stress at the interface, which improves films adhesion.

The effects of W buffer layer on the films growth, the hardness, and Young's modulus of the films were studied. In addition, the chemical bonding structures of the films were investigated by X-ray photoemission spectroscopy and near-edge X-ray absorption fine-structure spectroscopies to understand the physical origin of the films properties due to insertion of W intermediate layer.

３．実験内容（試料、実験方法、解析方法の説明）

WC–Co substrates (K-type cemented tungsten carbide) with a dimension of 10 × 4.5 mm were employed for film deposition. Only the pretreatment of roughening the substrates surface was chemically made in the roughness average range of 0.15–0.2 μm to enhance the adhesion of the films. Prior to the film deposition, the surfaces of the substrates were cleaned in acetone and methanol ultrasonic bathes for 7 min, respectively.

NDC films were deposited on WC-Co substrates at room substrate-temperature by CAPD with pure graphite targets. The inside of a vacuum apparatus was evacuated to base pressures of less than 10^{-4} Pa by a turbo molecular pump. An arc plasma gun equipped with a 720 µF capacitor was operated at an applied voltage of 100 V. The films were deposited directly and with sputtered W intermediate layer at various thicknesses as shown in Fig. 1. The hardness and Young's modulus of the deposited films were investigated by nano-indentation. The deposited films were characterized by X-ray photoemission spectroscopic at beamline 12 of Kyushu Synchrotron.

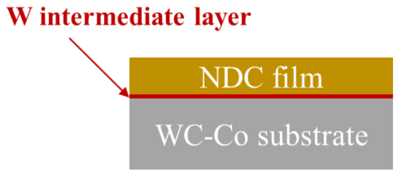

Fig. 1 schematic diagram of NDC films deposited on WC-Co substrates after insertion of W intermediate layer.

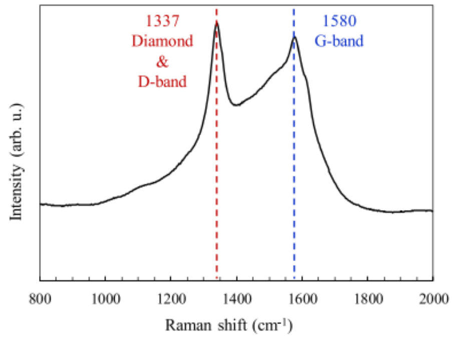

Fig. 2 Raman spectra of NDC films deposited on WC-Co substrates.

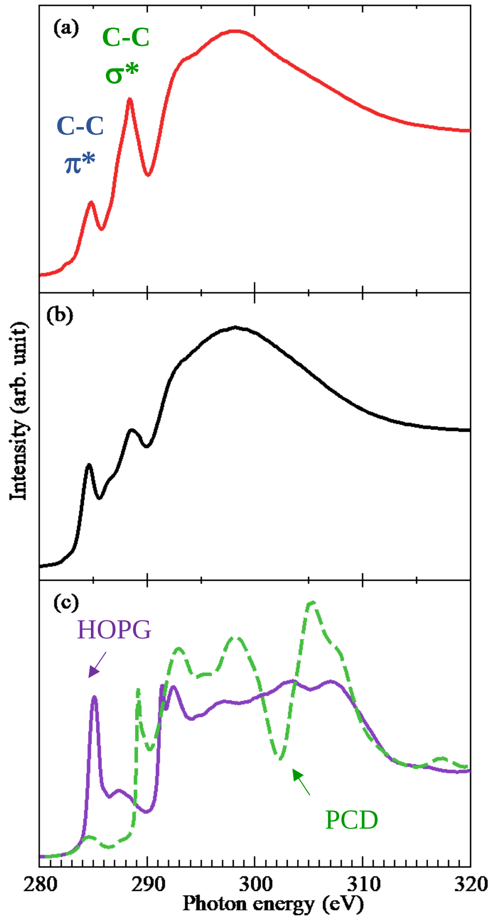

Fig. 3 C K-edge NEXAFS spectra of NDC films deposited on WC-Co substrate (a) with and (b) without W intermediate layer, and (c) reference spectrum of high oriented pyrolytic graphite (HOPG) and polycrystalline diamond (PCD).

４．実験結果と考察

The films deposited directly on WC-Co substrates exhibit a hardness of approximately 50 GPa and Young's modulus of 520 GPa. A Raman spectrum of the films is shown in Fig. 2. A peak detected at 1337 cm^{-1} might be due to UNCD grains. The peak position is slightly shifted from that of bulk diamond peak (1333 cm^{-1}) and its peak is broaden, which might be due to phonon confinement effects and scattering in nano-sized grains and due to the coexistence of D-band peak coming from a-C. Moreover, a broad peak around 1580 cm^{-1} was observed, which attributed to G-band of amorphous carbon matrices due to the bond stretching of carbon atoms in sp^2 hybridization. By the insertion of W intermediate layer, the hardness and Young's modulus were improved to 67.5 GPa and 719 GPa, respectively. This improvement might be attributed to the suppression of Co catalytic effects that induces films graphitization and in turn reduces films hardness and Young's modulus. Also, the adhesion between NDC film and WC-Co substrate was successfully enhanced due to the buffer layer enhanced the chemical compatibility between the film and substrate.

Figure 3 shows NEXAFS spectra of NDC films deposited with and without inserted W intermediate layer. The NEXAFS spectra show intense C-C $\sigma*$ peak to the films deposited on W intermediate layer comparable to the directly deposited films. The inserted W intermediate layer improved the diamond formation in the films, which enhances films hardness. Additionally, the center of $\pi*$ peak is shifted to the high energy side, which might be attributed to suppressing films compressive stress due to insertion of W intermediate layer.

５．今後の課題

This experiment shows the role of W intermediate layer in the suppression of Co catalytic effects, and the relationship between the film's hardness and C-C sp^3 fraction were investigated. The results demonstrated that the insertion of the buffer layer to form chemical compatibility can significantly increase the adhesion of NDC films on WC-Co substrates.

６．参考文献

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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, Raman, Hardness, NEXAFS, W intermediate layer

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）