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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

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

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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）

Ultrananocrystalline diamond/amorphous carbon composite (UNCD/a-C) films 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 UNCD/a-C 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. UNCD/a-C films were deposited by coaxial arc plasma deposition (CAPD) on cemented carbide (WC-Co) substrates directly and with tungsten (W) buffer layers. The films deposited on W buffer layers achieved an evident enhancement in the hardness to 56 GPa and Young's modulus to 593 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 buffer layers suppress Co catalytic effects that induces graphitization.

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. Ultrananocrystalline diamond/ amorphous carbon composite (UNCD/a-C) films deposited on WC-Co at room substrate-temperature exhibit the maximum hardness of 50 GPa and a 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 buffer layer was sputtered prior to the film deposition, because it was reported that the insertion of W buffer layer suppresses the catalytic reactivity of transition metals for inducing graphitization [2, 3]. 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 buffer layer.

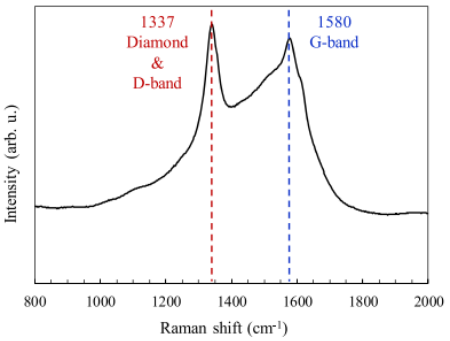

Fig. 1 Raman spectra of of UNCD/a-C films deposited on WC-Co substrates without W buffer layer.

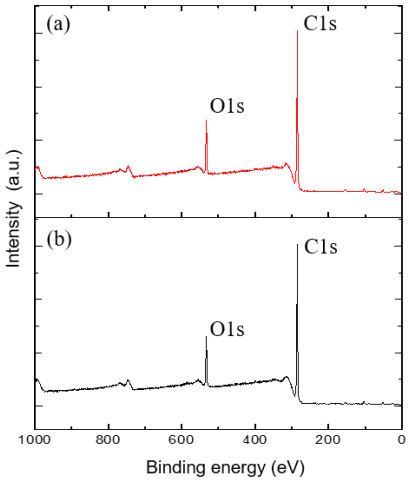

Fig. 2 XPS survey of UNCD/a-C films on WC-Co substrates (a) without and with W buffer layer.

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. The pretreatment by chemical etching for Co removal near the substrate surface, which has been essentially applied for the growth of CVD diamond coatings on WC–Co, was not carried out in this study. 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.

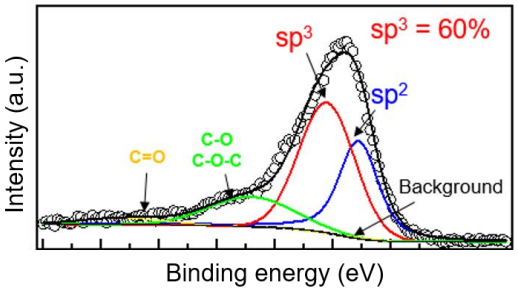

Fig. 3 C 1s X-ray photoemission spectra of UNCD/a-C films deposited without W buffer layer.

UNCD/a-C 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 W buffer layer sputtered at thickness of 100 nm. 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.

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. 1. 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 buffer layer, the hardness and Young's modulus were improved to 56 GPa and 593 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 UNCD/a-C film and WC-Co substrate was succesfly enhanced due to the buffer layer enhanced the chemical compatibility between the film and substrate.

Figure 2 shows the elemental composition of UNCD/a-C films measured by XPS survey. O 1s and C 1s peaks were detected, which indicates that the films are free of substrate contaminations. The O 1s peak is attributed to the residual oxygen in the chamber during the films preparation and exposure to the environmental air after deposition [4]. Figure 3 shows the X-ray photoemission spectra of UNCD/a-C films, which were decomposed to peaks by a software. The estimated $sp^3/(sp^3+sp^2)$ ratio is 60%, which show an agreement with the measured hardness and Young's modulus and Raman spectra.

５．今後の課題

In this work, the role of W buffer layer in the suppression of Co catalytic effects, and the relationship between the films 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 UNCD/a-C films on WC-Co substrates.

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, Raman, Hardness, XPS, X-ray photoemission spectroscopy, W buffer 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）