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バイアス印加基板に堆積した超ナノ微結晶ナノダイヤモンド膜の化学結合構造

Studies on chemical bonding structures of ultrananocrystalline diamond films deposited on cemented carbide substrates biased negatively

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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 were deposited on negatively biased cemented carbide (WC-Co) substrates by coaxial arc plasma deposition. The deposition rate is increased to be 0.9 nm/s, which is approximately 3 times larger than that of films deposited under no bias condition. In addition, the critical load in scratch tests was enhanced to be 31 N, which is 4 times more than that of the no bias films. On the other hand, the hardness was slightly degraded by employing the negative bias. From electrical diagnostics of the bias application, it was found that the negative bias is immediately compensated by the arrival of highly-dense positive carbon ions at the substrate and the substrate is weakly positively charged after the compensation. This might be the main reason for the degraded hardness by the bias application, Since the positive bias deaccelerate carbon ions, which facilities the formation of sp2 bonds.

２．背景と目的

The hardness, adhesion, wear resistance, smoothness, and maximum film thickness are important key factors for the hard coating applications. It is well known that negative bias application to substrates enhances their mechanical key factors, particularly the hardness and adhesion strength, of DLC films prepared by physical vapor de- position. Concretely, it was reported that the hardness increases by 10–20 GPa as compared with that of films without biases and the ad- hesion strength is apparently improved by applying high negative bias voltages to substrates [1–2]. In addition, the overall compressive stress in films decreases by applying biases to substrates, which results in the maximum film thickness to be deposited without being peeled off from the substrates.
On the other hand, there have a few research on the effects of negative bias application to UNCD/a-C films. Although it was reported that the formation of high-density nanocrystalline diamond (NCD) and UNCD on non-diamond substrates was achieved by bias enhance nucleation (BEN) and growth (BEG) for the deposition by microwave plasma CVD, the bias effects have never been studied for UNCD/a-C films prepared by CAPD thus far. In this work, to improve the mechanical key factors of UNCD/a-C films prepared by CAPD, negative

bias voltages were applied to WC-Co substrates, and the effect on the mechanical properties of the films were investigated. In addition, the electrical diagnostics was employed for investigating the bias process.

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 (purity 99.99%). A voltage of 100 V was applied to an arc plasma gun equipped with a 720 μF capacitor. The repetition rate of discharges was 1 Hz. A distance between a coaxial arc gun and the substrate was 15 mm. A substrate holder that was electrically isolated from the vacuum chamber of a CAPD deposition apparatus was connected to a Tru-Plasma Bipolar 4020 power supply, and quasi-DC bias of −100 V was applied in pulse with a duration of 8.7 μs at frequencies of 40, 60, and 80 kHz. The formation of UNCD grains in the deposited films was confirmed by Raman spectroscopy. 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.

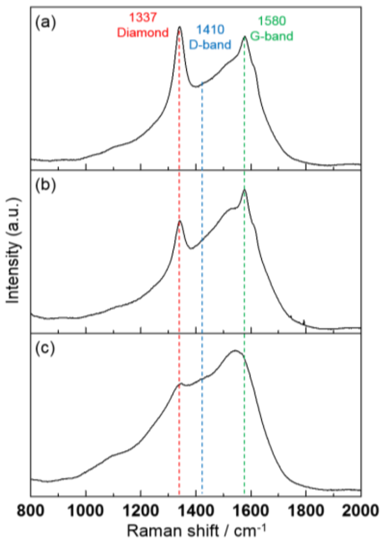

Fig. 1. Raman spectra of films deposited at (a) un-bias, and bias frequency of (b) 40kHz and (c)80 kHz.

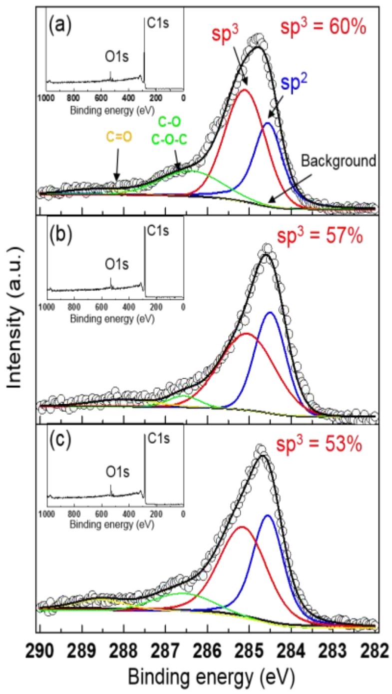

Fig. 2. Typical C1s X-ray photoelectron spectra of films deposited at (a) un-bias, and bias frequency of (b)40 kHz and (c)80 kHz. Inset show survey spectra.

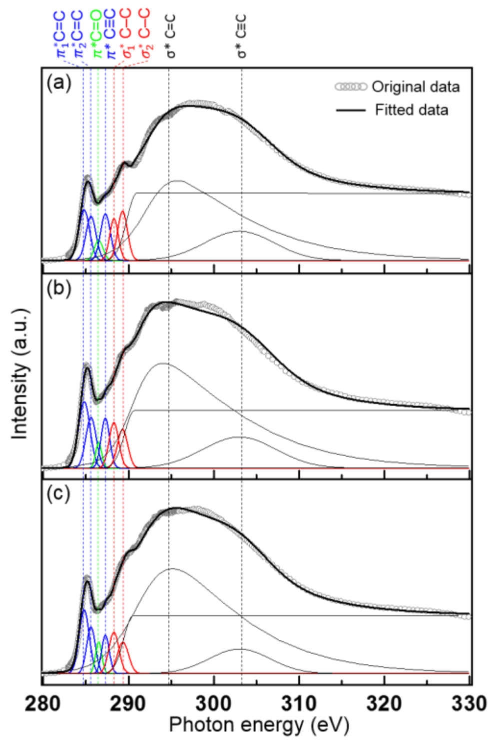

Fig. 3. Typical C1s X-ray photoelectron spectra of films deposited at (a) un-bias, and bias frequency of (b)40 kHz and (c)80 kHz. Inset show survey

４．実験結果と考察

It was found that The deposition rate of the UNCD/a-C films was drastically increased by the negative bias application. The deposition rate increases with increasing substrate current. Since the substrate current is attributed to the arrival of positively-ionized carbon species, this implies that carbon species ejected from the graphite cathode are almost positively ionized and they are attracted by the negative bias. The film thickness is in- creased to be approximately 9 μm without the film being peeled off from the substrate. Raman spectroscopy is a standard characterization technique for carbon system. Fig. 1 exhibiting the typical peaks associated with UNCD/a-C composited films. A distinct Raman band at 1337 cm^{-1} shows a typical behavior for diamond bonded of the deposited films.

X-ray photoelectron spectroscopy is an appropriate technique to assess the chemical composition of UNCD/a-C films. Fig. 2 shows X- ray photoemission spectra of the films deposited at different bias

frequencies measured using synchrotron radiation. The inset shows survey spectra measured with a MgKα line. Intense C 1s and O 1s peaks are observed at binding energies of 284.5 and 532.5 eV, respectively. To analyze the spectra more precisely, the C 1s spectra are decomposed into C=C (sp2), C-C (sp3), C-O, and C=O peaks with Voigt function after the backgrounds being subtracted by Shirley method. The sp3/(sp2 +sp3) ratio, namely sp3 fraction, was estimated from the areas of the decomposed sp3 and sp2 peaks.
NEXAFS measurements were examined to investigate the chemical structures of the films. NEXAFS spectra of the films deposited at no bias and different bias frequencies of 40 and 80 kHz are shown in Fig. 3. The spectra show sharp absorption due to π^* transition, and it was decomposed into peaks due to π_1^* C=C, π_2^* C=C, and π^* C≡C peaks located at photon energies of 284.8, 285.6, and 287.27 eV, respectively.

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. In addition, the results indicated from Raman spectroscopy strongly agree with that indicated from XPS and NEXAFS. The surface charge up phenomena was observed during the films deposition, 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.

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, Hard coating, Coaxial arc plasma deposition, CAPD, Raman, Nanoindentation, Soft X-ray spectroscopic, Si doping

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（2017 年度実施課題は 2019 年度末が期限となります)。

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① 論文（査読付）発表の報告　　　　（報告時期：　**2022** 年　**3** 月）