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ハードコーティング材料への応用特化した炭素皮膜の軟 X 線分光分析 II

Soft X-ray spectroscopic study on carbon films especially for hard coating applications II

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１．概要（注：結論を含めて下さい）

Si-doped ultrananocrystalline diamond/amorphous carbon composite (UNCD/a-C) films were deposited on cemented carbide (WC-Co) substrates for cutting tools applications by coaxial arc plasma deposition (CAPD). The UNCD/a-C films exhibit a hardness of 50 GPa and a modulus of 520 GPa. To improve the mechanical and tribological properties of the UNCD/a-C films further, the effects of Si doping was studied. Si-doped films deposited on WC-Co substrates directly showed a degradation in the mechanical properties due to graphitization induced by the diffusion of Co atoms from the substrates into the films. On the other hand, the Si-doped films with a 1-μm undoped UNCD/a-C buffer layers that block the diffusion of Co atoms into the films shows an enhancement in the hardness and modules. It was found that the amount of sp^3 bonds is evidently increased by Si doping from X-ray photoelectron and near-edge X-ray absorption fine-structure spectroscopic measurements while the diffusion of Co into the films is facilitated by Si doping.

２．背景と目的

Protective hard coatings to the WC-Co cutting tools are required in a variety of applications. 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.[1] The physical properties of carbon materials are strongly influenced by the ratio of sp^3 (diamond-like) to sp^2 (graphite-like) bonds[2]. The mechanical properties of ultrananocrystalline diamond (UNCD)/amorphous carbon (a-C) composite (UNCD/a-C) films comprising a large number of UNCD grains and an a-C matrix are expected to be strongly affected by the ratio between sp^3 and sp^2 bonds. In our previous study, we succeeded in the growth of 50 GPa hardness and 520 GPa Young’s modules UNCD/a-C films with a thickness of more than 3 μm by CAPD.[3] They exhibited the $sp^3/(sp^3+sp^2)$ ratio of 69%, which was estimated from X-ray photoemission measurements.[4]

Si atoms do not form sp^2 bonds but sp^3 bonds in the chemical bonding. Thus, in the case of Si doping is applied to carbon materials, it is expected that sp^3 bonds such as C-Si sp^3 bonds is preferentially formed.[5] In this work, the effects of Si doping on the deposition of UNCD/a-C films on WC-Co substrates was studied, and the chemical bonding structures of the films were investigated by X-ray photoelectron and near-edge X-ray absorption fine-structure spectroscopies.

３．実験内容（試料、実験方法、解析方法の説明）

Si-doped UNCD/a-C films were deposited on WC-Co substrates with dimensions of 10 mm diameter and 4 mm thickness at room temperature by CAPD with 1 at.% Si blended 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 140 V. Three types of structural films as shown in Fig. 1 were prepared. Concretely, Undoped UNCD/a-C films directly deposited on WC-Co substrate, Si-doped UNCD/a-C films directly deposited on WC-Co substrates, and Si-doped UNCD/a-C films deposited on approximately 1 μm undoped UNCD/a-C interlayers were prepared. The hardness and modulus of the deposited films were investigated by nano-indentation. The deposited films were characterized by nanoindentation, EDX, SEM, and soft X-ray spectroscopic at beamline 12 of Kyushu Synchrotron.

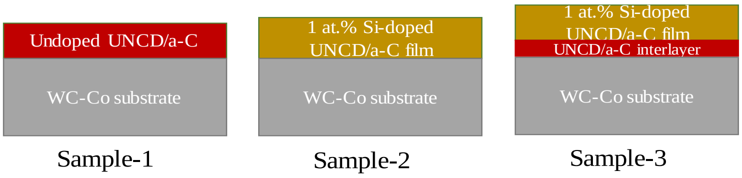

Fig.1 Schematic diagram of the deposited layers on WC-Co substrate

４．実験結果と考察

The undoped films (sample-1) deposited on WC-Co substrates exhibit a hardness of approximately 50 GPa and modulus of 520 GPa. From X-ray photoemission spectra as shown in Fig. 2, the sp^3 content was estimated to be 69%.

The Si-doped films (sample-2) directly deposited on the WC-Co substrates show a decrease in sp^2 content. Since the energy dispersive X-ray (EDX) spectra of the film exhibited that Co atoms diffused into the films from the substrates, this is probably because the Co atoms acts as catalysts that facilitate graphitization of sp^3 bonds. The Si-doped films with the interlayers exhibited no Co peaks in the EDX spectra as shown in Fig. 3, which implies that the interlayer effectively block the diffusion of Co atoms from the substrate. The sp^3 content was estimated to be 72% from the X-ray photoemission spectra, and the hardness and Young's modules were 60 and 610 GPa, respectively. It was found that Si doping evidently enhances the formation of sp^3 bonds, whereas it induces the diffusion of Co atoms from the WC-Co substrates, which results in degraded hardness and Young's modules..

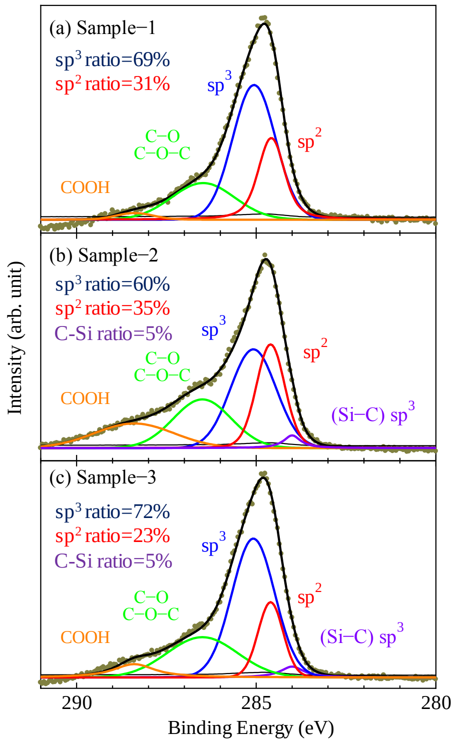

Fig.2 XPS C1s spectrum of Si-doped UNCD/a-C films

５．今後の課題

In this work, we could confirm the increased sp^3 content responsible for the enhanced hardness and Young's modules of the Si-doped films deposited on the interlayers. From this, we are going to the effects of Si doping on the internal stress of the films that is a key factor that determine the adhesion of the films on the substrates.

６．参考文献

1) A. Köpf , S. Feistritzer, K. Udier , Int. J. Ref. Metals & Hard Mat. 24, 354-359 (2006).
2) J. Robertson, Progress Solid State Chem. 21, 199-333 (1991).
3) Hiroshi Naragino et al. Appl. Phys. A, 122, (2016).
4) Hiroshi Naragino et al. Jpn. J. Appl. Phys55, 030302 (2016).
5) X. M. He et al. J. Vac. Sci. Tech. A, 18, 2143 (2000).

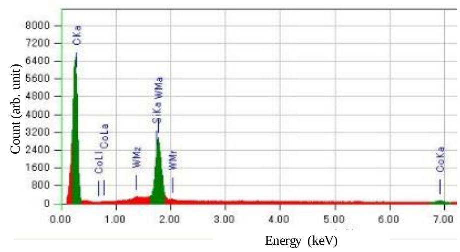

Fig.3 Top view EDX examination of Si-doped UNCD/a-C film (sample-2)

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）

- Hiroshi Naragino et al., Evergreen, 03, 1-5 (2016)
- Mohamed Egiza et al., Evergreen, 03, 32-36 (2016)
- Hiroshi Naragino et al., Jpn. J. Appl. Phys 55, 030302 (2016)

- Hiroshi Naragino et al. Appl. Phys. A, 122, (2016).

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, 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（2016 年度実施課題は 2018 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：2019 年　3 月）