同軸型アークプラズマ堆積法を用いた超ナノ微結晶ダイヤモンド/水素化アモルファスカーボン混相膜における放電周波数の影響

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(本文)

超ナノ微結晶/水素化アモルファスカーボン混相(UNCD/a-C:H)膜は，粒径 10 nm 以下のナノダイヤモンドと，水素化アモルファスカーボンから構成されており低摩擦係数，高い熱安定性，大きな吸収係数を有すことから，硬質被膜としても注目されている材料である．本研究では，同軸型アークプラズマ堆積法（CAPD 法）を用い，5-20 Hz の異なる放電周波数(R.R.)で作製した UNCD/a-C:H 膜の硬度と弾性率の評価を行い，SAGA-LS BL15 の粉末 XRD によりダイヤモンド粒径，BL-12 の NEXAFS を用い炭素の化学結合様式の評価を行った．硬度，弾性率共に 5 Hz で作製した時が最も高く，それぞれ 23GPa，184GPa を示し R.R の増加に伴い値が低下した.XRD のダイヤピークから見積もった粒径は 5Hz にて約 2.6 nm であり,R.R. 10 Hz,20 Hz では約 1.8 nm 程度であった．NEXAFS の測定結果から R.R の増加に伴いσ*C≡C ピーク，σ*C-H ピークの増加が観測されたことから，放電周波数の増加がダイヤモンド粒子の減少と，ダイヤモンド粒子界面への水素の取り込み量を増加させる効果を与え，膜を軟化させたと考えられる．詳細については当日報告を行う．

Influence of repetition rate of arc discharge on growth of ultrananocrystalline diamond/hydrogenated amorphous carbon films by using a coaxial arc plusma gun

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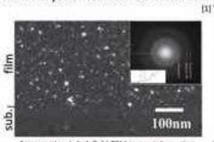
✱ Abstract

Ultrananocrystalline diamond/hydrogenated amorphous carbon composite (UNCD/a-C:H) films were prepared by using a coaxial arc plasma gun at different repetition rates of arc discharge. The influence of the repetition rate on the growth were structurally studied. With an increase in the repetition rate from 1 to 5 Hz, the UNCD crystallite size increased from 1.9 to 2.6 nm. The $sp^3/(sp^2 + sp^3)$ value estimated from the X-ray photoemission spectra also increased, which might be attributed to the enlarged UNCD crystallites. While the deposition by arc discharge occurs in pulsed process, the growth of UNCD crystallites takes place not independently but continuously.

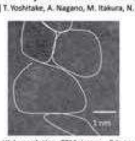
1. Introduction

Ultrananocrystalline diamond/hydrogenated amorphous carbon composite (UNCD/a-C:H) thin films, wherein non-oriented UNCD crystallites with diameters of approximately 5 nm were embedded in an a-C:H matrix [1], have attracted considerable interest from the physical and technological viewpoints, because of the following features; (a) some physical properties are similar to those of diamond and diamond-like carbon (DLC) due to sp^3 bonds; (b) a surface morphology is extremely smooth, which is similar to that of DLC and opposite to that of a polycrystalline diamond film; (c) they are thermally stable up to 550 ° C; (d) unique optical and electrical properties that might originate from a large number of grain boundaries (GBs) between UNCD crystallites and between UNCD crystallites and an a-C:H matrix.

[1] T. Yoshitake, A. Nagano, M. Itakura, N. Kuwano, T. Hara and K. Nagayama: Jpn. J. Appl. Phys. Vol. **46** (2007) L936.



Cross-sectional dark-field TEM image taken using the partial diffraction beam of diamond-111 and selected-area electron diffraction pattern (inset).



High-resolution TEM image. Fringes due to diamond-111 were observed. The diamond crystallite diameter was estimated to be approximately 5 nm.

	DLC	UNCD	Poly-crystalline diamond	Single-crystalline diamond
Structure	Amorphous	[illegible]	Poly-crystalline	Single-crystalline
[illegible]	◎	○	△	×
Temperature stability	×	○	○	○
Band gap	< 5.5eV	3.5eV?	5.5eV	5.5eV
Insulation	○	○	○	◎
Smoothness	◎	◎	×	◎
Heat conductivity	×	◎	◎	◎
Transparency	○	◎	◎	◎

Comparison of properties of DLC, UNCD and Diamond

2. Coaxial arc plasma deposition (CAPD)

UNCD/a-C:H films have mostly been fabricated by chemical vapor deposition (CVD), we have succeeded in fabricating them by coaxial arc plasma deposition (CAPD) wherein a coaxial arc plasma gun acts as a plasma source [2].

[2] T. Yoshitake, Y. Nakagawa, A. Nagano, K. Hanada, R. Ohtani, H. Setoyama, E. Kobayashi, K. Sumitani, T. Okajima, Y. Agawa, and K. Nagayama: Jpn. J. Appl. Phys. **49** (2010) 015503.

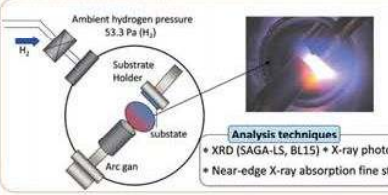
Specifics

- Few droplets.
- The ejected species are mainly ions.
- The crystallinity is enhanced due to highly energetic ion species.
- The supersaturated condition with highly energetic species can be realized in pulsed process.

3. Aim

In this study, we prepared UNCD/a-C:H films using a coaxial arc plasma gun at different repetition rates of arc discharges, and on the basis of the structural evaluation results, the influences of the repetition rate on the film formation is discussed

4. Experimental



condition

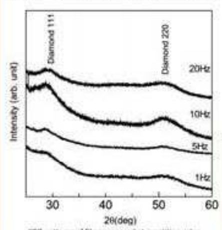
- Target : Graphite (99.99 %)
- Substrate : Si
- Temperature : 550 °C
- Repetition rate : 1 Hz to 20 Hz
- Capacitance : 720 µF
- Voltage : 100 V

Analysis techniques

- XRD (SAGA-LS, BL15)
- X-ray photoemission spectroscopy (SAGA-LS, BL-12)
- Near-edge X-ray absorption fine structure :NEXAFS (SAGA-LS, BL-12)

6. Result and Discussion

⋆XRD measurement



XRD patterns of films prepared at repetition rates of 1, 5, 10, and 20Hz.

•Diffraction intensity

Intensity of diamond-111 of the 5- and 10-Hz films have larger than those of the 1- and 20 Hz.

•Crystal size

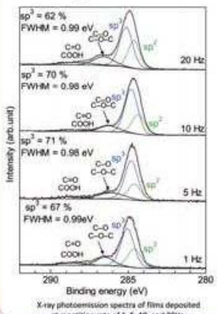
5-Hz and 10-Hz → 2.6 nm

1-Hz and 20-Hz → 1.9 nm

⇨ UNCD crystal size larger value at 5 and 10 Hz

Since the peak area and intensity of the 10-Hz film obviously larger than those the 5-Hz film, the 10-Hz film should contains a larger number UNCD crystallites in it. The 20-Hz film showed a broadened peak whose intensity was hardly reduced. This implies that the number of UNCD crystallites is hardly changed while the UNCD crystallite size is reduced.

⋆C1s photoemission spectrum



X-ray photoemission spectra of films deposited at repetition rate of 1, 5, 10, and 20Hz.

•$sp^3/(sp^2+sp^3)$

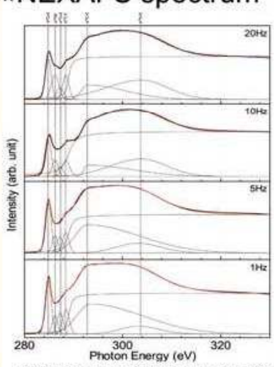
The 5- and 10-Hz films exhibited large values as compared to those of the 1- and 20-Hz films.

⇩

The large values of $sp^3/(sp^2 + sp^3)$ corresponds to the enhancement in the UNCD crystallite size.

Grain boundaries between UNCD crystallites and between UNCD crystallites and an a-C:H matrix should contains a lot of sp^2 bonds. On the other hand, the inside of UNCD crystallites is composed of sp^3 bonds. We consider that the enlarged UNCD crystallite results in the enhanced $sp^3/(sp^2 + sp^3)$ value, which is in good agreement with the experimental results.

⋆NEXAFS spectrum



NEXAFS spectra of films deposited at repetition rate of 1, 5, 10, and 20Hz.

NEXAFS spectrum ware decomposed with the component spectra due to π^*C=C, σ^*C-H, σ^*C-C, σ^*C=C, and σ^*C≡C.

C≡C peak and C-H peak have increased as the repetition rate increase from 1- to 20-Hz.

⇩

H-C ≡C-H structure increase with increasing repetition rate increase. C-H bonding present in grain boundary.[3]

[3] T. Yoshitake, A. Nagano, S. Ohmagari, M. Itakura, N. Kuwano, R. Ohtani, H. Setoyama, E. Kobayashi, and K. Nagayama: Jpn. J. Appl. Phys. **48** (2009) 020222.

This implies the grain boundary of diamond and diamond, or diamond and amorphous carbon become larger.

The experimental results that the UNCD crystallite growth is influenced by the repetition rate indicates that the UNCD crystallite growth keeps an activated state in interval periods between pulsed depositions caused by arc discharge. At a low repetition rate such as 1 Hz, the activated state must be lowered by a long interval time between arc discharges. Thus, the UNCD crystallite growth must be suppressed. On the other hand, at a high repetition rate such as 20 Hz, the UNCD crystallite growth after the nucleation might not afford to be progressed due to a short interval time (for example 50 ms for 20 Hz). In addition, a deposition amount of 1.33 nm/discharge corresponds to a huge effective deposition rate. This situation might also impede the crystallite growth after the nucleation.

8. Conclusion

We investigated the influence of a repetition rate of arc discharge on the growth of UNCD/a-C:H films. The UNCD crystallite size has a large value at 5 and 10 Hz. At smaller repetition rates, the UNCD crystallite growth including the nucleation might be inactivated due to a long interval time between arc discharges. On the other hand, at a higher repetition rate, the growth that successively occurs after the nucleation might be suppressed due to a short interval time and huge effective deposition rate.

Acknowledgments

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