Structure investigation of ultrananocrystalline diamond/amorphous carbon composite films in vacuum by a coaxial arc plasma gun

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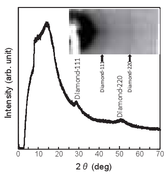
Abstract

Ultrananocrystalline diamond (UNCD)/non-hydrogenated amorphous carbon (a-C) composite films were grown in vacuum by using a coaxial arc plasma gun. From the X-ray diffraction measurement, the UNCD crystallite size was estimated to be 1.6 nm. The size is dramatically reduced from that (2.3 nm) of UNCD/hydrogenated amorphous carbon (a-C:H) composite films grown in a hydrogen atmosphere. The $sp^3/(sp^3 + sp^2)$ value, which was estimated from the X-ray photoemission spectrum, was also reduced to be 36%. A reason might be the reduction in the UNCD crystallite size. From the near-edge X-ray absorption fine-structure (NEXAFS) spectrum, it was found that the π^*C=C and π^*C≡C bonds are preferentially formed instead of the σ^*C–H bonds in the UNCD/a-C:H films. Since the extremely small UNCD crystallites (1.6 nm) correspond to the nuclei of diamond, we believe that the UNCD crystallite formation by CAPD should be predominantly due to nucleation.

UNCD Formation with Hydrogen Gas

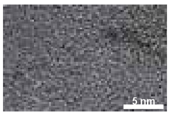
We realized the formation of ultrananocrystalline diamond/hydrogenated amorphous carbon composite (UNCD/a-C:H) films in hydrogen atmosphere by coaxial arc plasma deposition (CAPD).

XRD



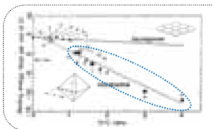
The inset shows the Debye-Scherrer ring image on the imaging plate.

TEM image



A UNCD crystallite size was estimated to be 2.3 nm.

Hydrogen Gas Effect on the UNCD Formation



In the case of the dangling bonds of carbon clusters with diameters less than 3 nm being terminated by hydrogen, the tetrahedral (diamond) structure is more stable than hexagonal one.

* P. Badziag, W. S. Verwoerd, W. P. Ellis and N. R. Greiner, Nature 343 (1990) 244-245.

Hydrogen stabilizes the sp^3 hybridization of carbon atoms at the diamond surface.

* M. Frenklach, H. Wang, Phys. Rev. B 43 (1991) 1520.

Atomic hydrogen is involved in the most surface reaction and facilitates the incorporation of carbon atoms into diamond lattices, which results in the enhancement in the deposition rate and crystalline quality.

* D. G. Goodin and J. E. Butler, In *Handbook of Industrial Diamonds and Diamond Films*, edited by M. A. Prelas, G. Popovici, and K. Bigelow (Dekker, New York, 1997) p. 527.

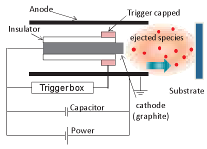
Hydrogen atoms remove non-diamond carbon from the surface.

* B. V. Spitsyn, L. L. Bouilov, and B. V. Derfaguin, J. Cryst. Growth 52 (1981) 219.

A hydrogen atmosphere might have significant roles on the UNCD formation.

Coaxial Arc Plasma Gun

Operation image



Specifics

- The ejected species are *mainly ions*.
- *sp^3-righ carbon films* can be deposited.
- Pulsed process makes contribution to *a supersaturated condition*.
- An anordic cylinder can bunch ion species, which contributes to *a supersaturated vapor* with highly energetic ions preferable for UNCD growth.

Aim: We attempt to grow UNCD/*a*-C films in vacuum by a coaxial arc plasma gun using a graphite target.

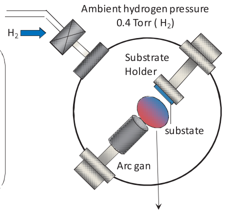
Experimental Method

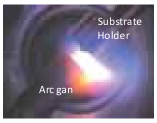
condition

Target	Graphite
Substrate	Si
Temperature	550 °C
Repetition rate	5 Hz
Number of pulse	300 pulse
Depo.speed	1.46 nm / pulse
Capacitance	720 µF
Votage	100 V

Analysis techniques

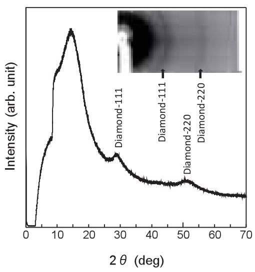
XRD (SAGA-LS, BL15)
AFM
NEXAFS (SAGA-LS, BL12)
Photoemission spectroscopy (SAGA-LS, BL12)





X-ray Diffraction Pattern (XRD)

(with Synchrotron radiation)



The inset shows the Debye-Scherrer ring image on the imaging plate.

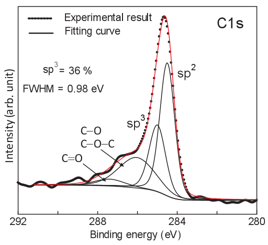
UNCD Crystallite Size
- UNCD/a-C film : 1.6 nm
- UNCD/a-C:H film : 2.3 nm

A hydrogen atmosphere facilitates UNCD crystallite formation. However, it is not essential.

The extremely small crystallites (1.6 nm) should correspond to nuclei of diamond.

SR – Photoemission Spectroscopy

(with Synchrotron radiation)



The background was subtracted using Shirley's method.
The spectrum was decomposed using Voigt functions.

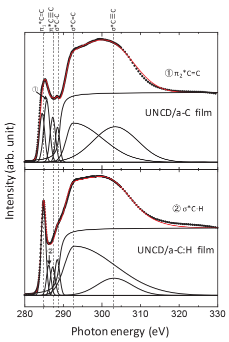
The C-O / C-O-C and C=O / COOH peaks originated from the film surface; they disappeared after ion bombardment effecting.

A large $sp^3/(sp^2 + sp^3)$ value
- UNCD/a-C film : 36 %
- UNCD/a-C:H film : 64 %

This difference should be attributed to the diminished UNCD crystallite size.

Near-Edge X-ray Absorption Fine Structure (NEXAFS)

(with Synchrotron radiation)



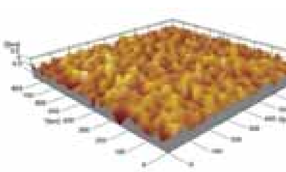
UNCD/a-C film
- π^*C=C and π^*C≡C peaks are broadened
- π^*C=C is divided into two : π_1^*C=C and π_2^*C=C
- π^*C≡C peak is stronger

UNCD/a-C:H film
- σ^*C-H peak is observed

Instead of the σ C–H bonds, the π C=C and π C≡C bonds are preferentially formed in vacuum.
These results are consistent with the reduced $sp^3/(sp^2 + sp^3)$ value.

Atomic Scope Microscope (AFM)

Atomic Force Microscope (AFM)



RMS roughness is approximately 0.2 nm
Film surface is extremely smooth compared with the UNCD crystallite size.

UNCD crystallite formation is realized at subsurface rather than film surface.

Conclusion

- We succeeded in growing UNCD/*a*-C composite films in vacuum by the coaxial arc gun.
  UNCD crystallite size
  - UNCD/a-C film : 1.6 nm
  - UNCD/a-C:H film : 2.3 nm

  → UNCD formation in vacuum by CAPD should be predominantly due to nucleation.
  Hydrogen facilitates UNCD growth.
- A smaller $sp^3/(sp^2 + sp^3)$ value (36%) was obtained as compared with that of UNCD/a-C:H films.
  → This might be attributed to *the diminished UNCD crystallite size.*
- Two peaks of π^*C=C & a stronger π^*C≡C peak were observed in UNCD/a-C films, while σ^*C-H peak was observed in UNCD/a-C:H films.
  → Instead of the σ C–H bonds, the π C=C and π C≡C bonds are preferentially formed in vacuum.
- The RMS was 0.2 nm.
  → *UNCDs are generated on not the surface but the subsurface of the film.*

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