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Chemical Bonding Structural Analysis of Nitrogen-Doped Ultrananocrystalline Diamond/Hydrogenated Amorphous Carbon Composite Films Prepared by Coaxial Arc Plasma Deposition

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Abstract

Nitrogen-doped ultrananocrystalline diamond/hydrogenated amorphous carbon composite films prepared in hydrogen and nitrogen mixed-gas atmospheres by coaxial arc plasma deposition with graphite targets were studied electrically and chemical-bonding-structurally. The electrical conductivity was increased by nitrogen-doping, accompanied by the production of n-type conduction. From the near-edge X-ray absorption fine-structure, hydrogen forward-scattering, spectral results, it is expected that hydrogen atoms that terminate diamond grain boundaries are partially replaced by nitrogen atoms and resultantly π C-N and C=N bonds that easily generate free electrons are formed at grain boundaries.

1. Introduction

Ultrananocrystalline diamond/hydrogenated amorphous carbon composite film (UNCD/a-C:H) is a new candidate carbon semiconductor, and the application to electrical devices has received much attention[1].

It has been known that nitrogen-doping for single crystal diamond is ineffective for realizing n-type conduction at room temperature because nitrogen form a deep donor level of 1.7 eV below the bottom of the conduction band in diamond. For a-C, n-type conduction is realized by nitrogen incorporating, however it is difficult for the carrier density to be controlled widely. On the other hand, it has been reported that nitrogen incorporating makes possible n-type conduction accompanied by an enhancement in the carrier density for UNCD/a-C:H films prepared by chemical vapor deposition (CVD) and physical vapor deposition (PVD) such as pulsed laser deposition (PLD) and coaxial arc plasma deposition (CAPD). Growth of UNCD/a-C:H has been commonly used by CVD with diamond powder seeding. On the other hand, UNCD crystallites can be grown by PLD and CAPD without seeding, because of high density of energetic carbon species, such as C^+ ions, is introduced during the deposition process. Especially, in case of CAPD, the electrons and the energetic carbon ions generated by the discharge for unlike cathodic arc deposition of the conventional, it is the cancer of the coaxial structure accelerated toward the substrate by the magnetic field generated by the large current flowing in the axial direction of the cathode target it is can be supplied onto the substrate to selectively energetic ion particles. At this time,

the voltage applied mainly, the energy supplied to the cathode target is a device very simple configuration can be controlled by electric control. UNCD growth rate even faster overwhelmingly compared with other method and 400 nm/min, it is suitable for engineering applications.

Therefore, we focus attention on it as a new deposition technique instead of CVD and PLD. So far, fabricating UNCD/a-C:H by CAPD is possible in the hydrogen atmosphere and vacuum and it has been confirmed p-type conduction by doping boron[2]. Therefore, creation of n-type UNCD/a-C:H film is significant from view point of new electrical devices. Although it has been experimentally demonstrated n-type UNCD/a-C:H film prepared by CAPD under hydrogen and nitrogen mixture gas atmosphere[3], its origin has not been investigated enough yet. Thus, in this study, chemical bonding structures of nitrogen doped UNCD/a-C film fabricated by CAPD were studied by spectroscopic analysis.

2. Experimental Methods

Undoped and nitrogen doped UNCD/a-C:H films with a thickness of approximately 300 nm were deposited by CAPD at a substrate temperature of 550°C and an ambient hydrogen and nitrogen mixture gas pressure of 53 Pa as shown in Fig. 1. Inflow ratio of hydrogen and nitrogen (I_{NH}) was set 0 and 0.25. The quartz and p-type Si (100) were used as substrates for the evaluation of electrical conductivity and chemical bonding configurations, respectively. Temperature dependence of electrical conductivity on undoped and nitrogen doped films were evaluated by van der Pauw method. NEXAFS was used to analyze details of chemical bonding

structures in UNCD/a-C:H films at beamline 12 (BL12) of the SAGA-LS. The hydrogen content was quantitatively measured by hydrogen forward-scattering spectroscopy (HFS). The measurements were outsourced to the Foundation for the Promotion of Material Science and Technology of Japan, and the measurements were performed using a Rutherford back-scattering apparatus with a 2.275 MeV 4He^{++} ion beam under an incident angle of 30° .

3. Result and Discussion

Figure. 1 shows the temperature dependence of the electrical conductivities ranging 500 to 300 K on undoped and nitrogen doped films. Conductivity of each film was decreased with decreasing temperature so that means both films are semiconducting film and their conductivity were obtained the value of 10^{-6} and 10^{-3} S/cm order, respectively. And the electrical conductivity was increased 10^3 order with nitrogen-doping. Activation energy (E_a) of undoped and nitrogen doped films were estimated approximately 360 meV and 100 meV, respectively. The reason of decreasing E_a is predicted that mid-gap state caused by hydrogen and dangling bond is expanded to conduction band side by replacing them to nitrogen atoms.

The C K-edge NEXAFS spectra of undoped and nitrogen doped films are shown in Fig. 2. In case of nitrogen doped film, it was exhibited three additional component spectra compared with the undoped film. The spectra with peak positions at 286.8, 289.2 and 297.8 eV are probably due to $\pi^*C=N$, σ^*C-N and $\sigma^*C=N$. Since two dimensional bonding was not formed in nano-sized diamond grain, it suggests that these bonding are preferentially formed at diamond grain interfaces or grain boundaries and they work as donor. The absolute hydrogen content of the undoped and nitrogen-doped films were estimated by HFS spectroscopy. From the HFS spectra shown in Fig. 3, the hydrogen content was estimated to be 35 at. % for the undoped film and 18 at. % for the nitrogen-doped film, respectively, using simulation software. The hydrogen content is evidently decreased by nitrogen doping.

4. Conclusion

Totally considering the NEXAFS and HFS results, it is expected that doped nitrogen atoms preferentially exist at GBs and form π C-N and C=N bonds that are sources of carriers. This does not contradict the previous reports on n-type conduction in nitrogen-doped nanodiamond films prepared by CVD.7) Although nitrogen-doped UNCD/a-C:H films prepare by CAPD seems to contain a large amount of a-C:H as compared with

CVD nanodiamond films, the production of n-type conduction accompanied by an enhancement in the electrical conductivity is probably similarly realized.

References

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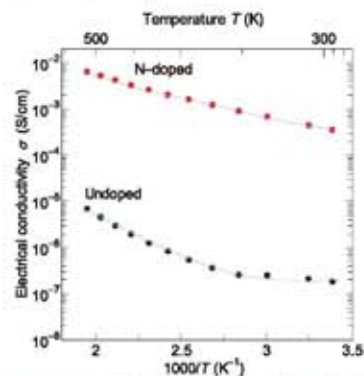


Fig. 1. Temperature dependence of electrical conductivity of undoped and nitrogen-doped UNCD/a-C:H films.

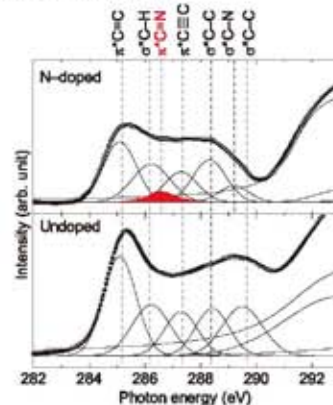


Fig. 2. C K-edge NEXAFS spectra of undoped and nitrogen-doped UNCD/a-C:H films.

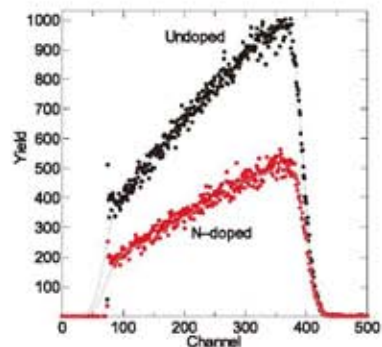


Fig. 3. Hydrogen forward-scattering spectra of undoped and nitrogen-doped films.