Spectroscopic study on boron-doped ultrananocrystalline diamond thin films synthesized by coaxial arc plasma: Toward the application to UV photodetector

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Ultrananocrystalline diamond (UNCD) thin films are generally synthesized by various chemical vapor deposition (CVD) techniques, however we have developed another method, so-called coaxial arc plasma deposition (CAPD) method ever since it was realized in 2010.[1)] The former is a well-known technique in the fabrication of a variety of semiconductor devices, such as transistors, solar cells, and LEDs. CVDs synthesize quite dense diamond crystallites by seeding pretreatments of substrates under ambient Ar, CH_4, and/or C_2H_4 gases. On the other hand, CAPD can prepare films comprising UNCD grains and hydrogenated amorphous carbon (a-C:H). They possess a lot of grain boundaries (GBs), which denote interfaces between UNCD grains and those between UNCDs and an a-C:H matrix.[1)] This structural difference would produce specific physical properties, for example, extremely large light absorption coefficients excessing 10^5 cm^{-1} in the photo range of 3 to 6 eV, which are at least two orders of magnitude larger than those prepared by CVDs.[1)] These are especially preferable to the application to UV sensors. In our previous research, p- and n-type conductions of UNCD/a-C:H films by doping boron[2)] and nitrogen[3)] were experimentally demonstrated and pn heterojunction diodes were realized by combining them with n-[2)] and p-type[3)] Si substrates, respectively. Fundamental studies aiming at applications to the photodiodes have been accumulated up to date, and we concluded the dopants[2-6)] and hydrogen[7-9)] incorporated in the films would have significant influences on their morphology and their photovoltaic performances. However, there have been few reports on the obvious evidence of the effectiveness of hydrogenation thus far. In this work, we report extensively that the boron-doping effects on the films from the viewpoints of chemical bonding structure by use of X-ray photoemission spectroscopy, Near-edge X-ray absorption fine structure (NEXAFS), and Fourier transform infrared spectroscopy (FT-IR) spectra at the beginning. And finally, we demonstrate distinct morphological phenomena totally different from conventional CVD diamonds and DLCs, by means of the same measurements employed to the films with different hydrogen contents.

An undoped and four B-doped UNCD/a-C:H films were prepared by CAPD with undoped, and 0.1, 1.0, 5.0, 10 at. % B-contained graphite targets to investigate the B-doping effects on the films. The detail process is referred to Ref. 2. Hydrogen contents in the films might be controllable by changing applied voltage to the gun, and we employed 70, 85, 100, and 115 V this time. The detail mechanism and process are described in Ref. 9. XPS and NEXAFS measurements were conducted at beamline 12 of Kyushu Synchrotron Light Research Center. Mg Kα line ($h\nu$ = 1253.6 eV) and 350 eV X-rays were employed as light sources in XPS and NEXAFS analysis.

X-ray photoemission wide-range spectra exhibit strong peaks at around 280 and 530 eV, originating from C 1s and O 1s, respectively as shown in Fig. 1(a). This means the existence of UNCDs and/or a-C:H. B incorporation into the films are certainly realized as Fig. 1(b) indicates while involving oxygen atoms as Fig. 1(c) does.

Figure 2 shows normalized X-ray photoemission C 1s spectra of B-doped UNCD/a-C:H films prepared by a B 1.0 at. % blended target with presumably different hydrogen contents after subtracting the charge-up effects properly, and the original spectra are displayed in the inset. All of their spectra are overlap with each other except for that of the films prepared with 100 V. However, this energy shift is negligibly small referring to the difference of binding energy between sp^2 and sp^3 carbon hybridization in UNCD films is 0.5 eV at most.[10)] Since the spectra are able to sensitively reflect hydrogenation to UNCD grain surfaces and an a-C:H matrix, this result implies that hydrogen atoms are preferentially localized at GBs. This chemical bond transition by additional hydrogenation is entirely different from those of diamonds synthesized by conventional CVD techniques, in which carrier transport are conducted through their extremely smooth grain surfaces terminated by hydrogen atoms, so-called "transfer-doping model". A probable reason for it is our nano-structured UNCDs are highly close to disordered composite materials rather than crystalline ones, which are structurally different from those by CVDs. The extra discussion of deconvoluted spectra and the other spectroscopic studies will be reported at the conference.

1) T. Yoshitake *et al.*, *JJAP*, **49** (2010) 015503., 2) Y. Katamune *et al.*, *JJAP*, **52** (2013) 065801., 3) A. Zkria *et al.*, *APEX*, **8** (2015) 095101., 4) Y. Katamune *et al.*, *JJAP*, **51** (2012) 078003., 5) A. Zkria *et al.*, *JJAP*, **55** (2016) 07LE01., 6) H. Gima *et al.*, *APEX*, **10** (2017) 015801., 7) Y. Katamune *et al.*, *J. Vac. Sci. Technol. A*, **33** (2015) 061514., 8) Y. Katamune *et al.*, *Trans. Mater. Res. Soc. Japan*, **40** (2015) 243., 9) N. Nishikawa *et al.*, *Trans. Mater. Res. Soc. Japan*, **43** (2018) 361., 10) S. Ohmagari *et al.*, *Diam. Relat. Mater.* **19** (2010) 911.

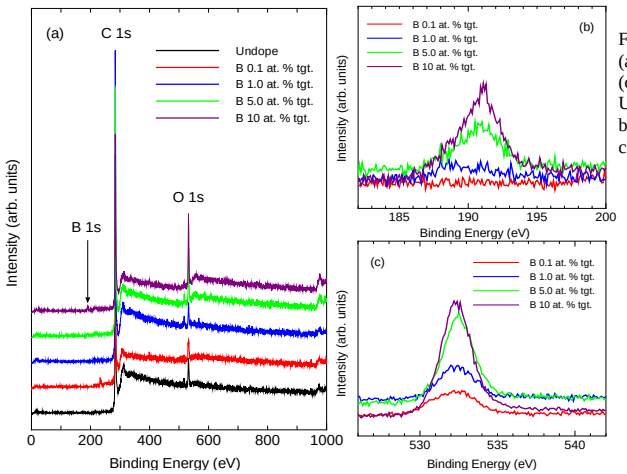

Fig. 1. X-ray photoemission (a) wide-range scan, (b) B 1s, (c) O 1s spectra of B-doped UNCD/a-C:H films prepared by different amounts of boron contained targets.

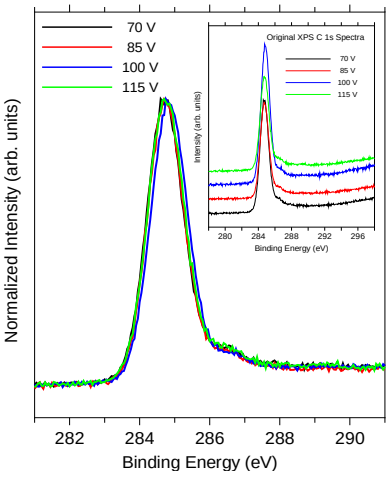

Fig. 2. Normalized X-ray photoemission C 1s spectra of B-doped UNCD/a-C:H films with different applied voltage to the gun. The inset shows their original spectra.