BL-5

Metallization of boron-doped amorphous carbon films

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Keywords: Metallization, Boron doped, Amorphous carbon, Film

Amorphous carbon (a-C) has excellent mechanical properties such as high hardness, high corrosion resistance, and low friction coefficient, and is therefore used as a coating material for automotive parts, molds, cutting tools, etc. On the other hand, the electrical properties of a-C are insulating, which makes it difficult to utilize this material for electrical devices. If a-C can be made conductive, a-C expands its application fields including electronics devices. Impurity doping is an effective approach to obtain the conductive a-C. However, metallic a-C has not yet been realized due to the presence of a high defect density that suppresses the carrier generation efficiency in a-C.

Q-carbon, a new allotrope of carbon, is discovered in 2015 [1]. This material is amorphous and consists of 80% sp^3 bonds and 20% sp^2 bonds. Interestingly, when Q-carbon is doped with boron, it becomes superconducting with the transition temperature of 36 K at boron-doping level of 17% [2]. This indicates that the boron-doped a-C can be metallic, and also that the carrier generation efficiency in the boron-doped Q-carbon is an order of magnitude higher than that of conventional a-C. Boron-doped Q-carbon provides a promising way for realizing the metallization of a-C.

Boron-doped Q-carbon is formed in a non-equilibrium process. This material is produced by the pulsed laser deposition of the amorphous film with boron and a-C mixture and subsequent pulsed laser annealing (PLA) of the B and C mixed films at room temperature and pressure in air, using a nanosecond pulsed UV excimer laser. During PLA, the films are melted to a highly undercooled state and subsequently rapid quenched to room temperature Since the duration of PLA is about only 200 ns, it is important to properly control the heat in quite short time to obtain this material. We have previously developed an adjusted pulsed laser annealing (adjusted PLA) method that allows thermal control through experimental parameters, and obtained the non-doped Q-carbon [3]. In this study, the boron-doped a-C films were prepared using the adjusted PLA method, and study on the electronic states were performed to investigate the metallic nature of the obtained films.

Starting material films of boron and a-C mixture (hereafter as-deposited films) were prepared on Al_2O_3(0001) substrates by using a pulsed laser deposition technique with a Nd:YAG laser (λ= 355 nm, τ = 5 ns). The film deposition was carried out at a substrate temperature of 300 K under a vacuum condition of 3×10^{-8} Torr. The film thickness is 150 nm, and the B/C ratio in the film is 35%. PLA was performed on the staring material films at ambient atmosphere and temperature using the Nd: YAG laser. The films with PLA (hereafter PLA-films) were obtained by irradiating one laser pulse through a converging lens to the surface of the starting material films. The energy density of PLA was set to 0.6 J/cm^2. The as-deposited and PLA-films were characterized by using synchrotron radiation photoelectron spectroscopy (PES) at HiSOR BL-5 and SPring-8 BL25SU. Monochromated X-ray of 700 and 1300 eV was used for measurements and the total energy resolution was set to about 80 and 170 meV for 700 and 1300 eV, respectively in the measurements at SPring-8 BL25SU. Before measurements, the samples were annealed at 120 ^{o}C under vacuum condition of 5×10^{-7} Pa for 30 min to obtain a clean surface. The Fermi level position was determined by measuring the Fermi edge of gold. All spectra were taken at 300 K.

Figure 1 shows the valence band spectra of the as-deposited and PLA-films. For the as-deposited film, the

valence band spectrum shows a broad structure. A fairly broad, intense peak located between 16 and 19 eV is mainly due to carbon 2*s* band, a broad shoulder located at about 11 to 14 eV is mainly due to the mixture of carbon 2*s* and 2*p* bands, and a very broad and decidedly weaker structures extending from 10 eV to the cutoff energy is mainly due to carbon 2*p* band. A broad peak at about 25 eV is due to the O 2*s* band which is a result of contamination in the film preparation process. The obtained result is in good agreement with that of amorphous carbon films reported previously [4]. For the PLA-film, the shape of valence band spectrum is similar to that of the as-deposited film. However, there is a difference between two spectra; the broad structure from 4 eV to the cutoff energy is more obvious in the PLA-film. This suggests that the valence band spectrum is changed by PLA. In order to see the top of valence band spectrum in more detail, the near Fermi level spectra of both as-deposited and PLA-films were collected. The result is shown in Figure 2. A finite intensity is observed at the Fermi level for the PLA-film, while it is not for the as-deposited film. This indicates that the PLA-films becomes metallic after PLA. The PES spectra of boron 1s core-level of the PLA-films is drastically changed compared to that of the as-deposited films (not shown), indicating that the boron atoms are incorporated in the PLA-films. The XPS measurements of valence band and B 1*s* core-level reveal that the film becomes metallic due to the boron doping by PLA. We will present the results of spectral analysis of C 1*s* and B 1*s* core-levels in both as-deposited and PLA-films.

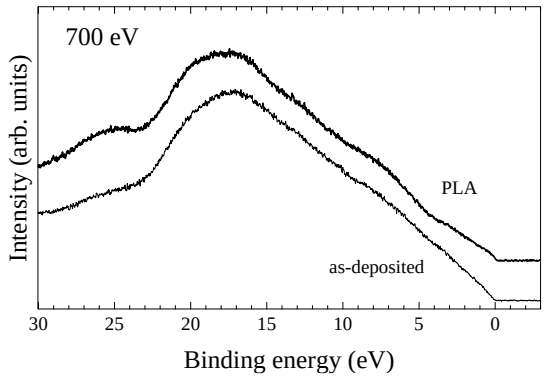

FIGURE 1. Valence band spectra for the as-deposited and PLA-films measured with a photon energy of 700 eV at 300 K.

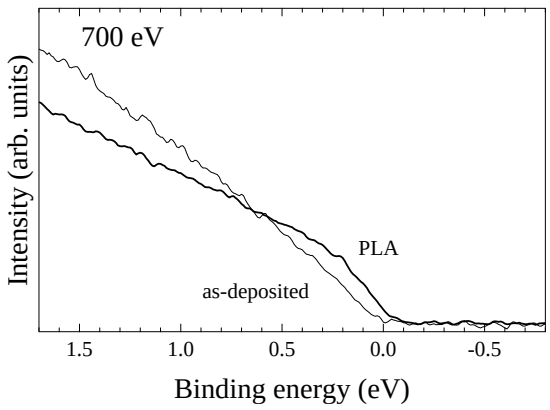

FIGURE 2. Near Fermi level spectra for the as-deposited and PLA-films.

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