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Preparation of double layer film of boron and carbon by pulsed laser deposition

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Abstract

Double layer films of boron and carbon were prepared by pulsed laser deposition (PLD) on silicon substrates. The film surface morphology was examined by atomic force microscopy (AFM). The chemical composition of the elements, carbon, boron, silicon and oxygen, and bonding state of carbon atoms as a function of the depth from the film surface were analyzed by X-ray photoelectron spectroscopy (XPS) with argon ion sputtering technique. Carbon atoms bonded to boron (C-B) were observed as well as carbon atoms bonded to carbon (C-C).

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1. Introduction

Recently, properties of high yield and lower voltage threshold for field electron emission from carbon materials, which are attributed to its low electron affinity, have attracted attention for an application of electron emitters in flat panel displays [1-3]. The authors, as well, are interested in amorphous carbon (a-C) films as an electron emission material because a-C film can be fabricated in large size at low cost and has the possibility to enhance emission properties by boron or nitrogen doping [2, 3].

In this paper, we report the preparation of double layer film of boron and carbon by pulsed laser deposition (PLD). PLD is a powerful technique to deposit thin films directly from solid target materials and to control energy and amount of ablated materials. Atomic force microscopy (AFM) was used to examine the film surface morphology. X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical composition at different depth of the film.

2. Experimental

2.1. Experimental setup and procedure

The experimental setup is described in a previous report [4]. Briefly, the deposition chamber contains a substrate and six target holders and is evacuated up to 2.7×10^{-6} Pa. ArF excimer laser beam (λ = 193 nm; τ = 20 ns; repetition rate = 10 Hz; laser fluence = 2.5 Jcm^{-2}) was irradiated on the target located 35 mm away from the substrate. Sintered carbon (99.999% purity) and boron (99% purity) targets rotated at 25 rpm were used. A substrate was *p*-type Si (111) (40 – 60 Ωcm) and was rinsed in a solution of hydrofluoric acid for 5 min to eliminate native oxide layer. We introduced a mask with a 10-mm square hole between the target and substrate. In this experiment, carbon film was previously deposited on

substrate by PLD in oxygen plasma ambience as reported in [5], and then boron was deposited over the carbon film in vacuum for 5 – 240 min. All the experiments were carried out at room temperature.

2.2. Characterization of film property

The surface morphology on the carbon and boron-deposited carbon film was examined with an AFM (Digital Instruments Nanoscope III Dimension 3000). The chemical composition and bonding state of the films were analyzed by an XPS (Shimadzu ESCA-3400) with a monochromated Mg K_α (1253.6 eV) X-ray radiation and analyzer pass energy of 75 eV. The XPS spectra of C 1s, B 1s, O 1s and Si 2p were decomposed with Gaussian curves to evaluate the chemical composition. After the XPS analysis, the film was sputtered by argon ion beam irradiation (acceleration voltage: 2 kV; ion current: 20 mA) for ~120 s, and then the exposed surface was analyzed. This sequence was repeated until the Si 2p spectra of the substrate appeared.

3. Results and Discussion

3.1. Surface morphology

Fig. 1 shows the AFM image of the film surface: (a) carbon film deposited in oxygen plasma ambience [5] and (b) the film after boron was deposited for 120 min on film (a). Nanometer-size particles (nanoparticle) were seen on film (a). The average particle height was ~ 8 nm, which was obtained from the sectional view of the AFM image, as performed in [6]. On film (b), the entire surface was covered by larger domains compared with the particles in film (a). It is seen that boron covered the carbon nanoparticles and accordingly the domain size increased.

Fig. 1. AFM images of the films: (a) carbon film surface prepared by PLD in oxygen plasma [5]; (b) boron-deposited surface on the film shown in (a).

3. 2. Analyses of film property and chemical composition

The chemical composition of the film obtained for different boron deposition times was evaluated by the XPS as shown in Fig. 2. The Boron concentration was shown to increase linearly with the deposition time.

Fig. 2. Chemical composition of C, B, O and Si by the XPS spectra as a function of the boron deposition time.

Fig. 3. The C (1*s*) XPS spectra of the boron-deposited carbon film for different Ar^+ sputtering time (t_s). Decomposed spectra of C (1*s*) at t_s = 600 s are shown.

The C 1s XPS spectra of the boron-deposited carbon film, on which boron was deposited for 240 min, for various sputtering time (t_s) are shown in Fig. 3. The XPS instrument was calibrated by peak binding energy of Ag 3d to be 368.1 eV. After the film surface was sputtered by Ar^+ for 3500 s altogether, Si 2p spectra of the substrate appeared. Since the analysis was not performed in situ, the top surface of the film would contain carbon oxide. In the spectra of the film sputtered for 15 s two peaks of C-C and C-B bonds are clearly seen. At t_s = 600 s, the spectra changed to have broad structure with a full-width at

Fig. 4. Chemical composition of C, B, O and Si by the XPS spectra as a function of t_s.

half-maximum (FWHM) of ~2.8 eV, which may indicate that the spectra contain C-C and C-B bond (the peak binding energy is 282.9 eV) [7]. The B 1s spectra of the film also contained two different components (not shown in the text), B-B bond (the peak binding energy is 188.6 eV) and B-C bond (190.6 eV) [7]. The C 1s spectra was deconvoluted into four components as similarly performed in [5]; C-C (sp^3 bonded, 285.5 eV, sp^2 bonded, 284.1 eV), C-B and unidentified C component ascribe to bond disorder in an amorphous structure as shown in Fig. 3. As t_s increased, the C-B bond component in the C 1s spectra decreased promptly as compared with the C-C one, and in the B 1s spectra the B-B component decreased promptly as compared with the B-C one. These results suggest that inside the film the chemical bond between carbon and boron atom exists. Considering a sub-plantation model [8], it is reasonable that ablated boron atoms with high kinetic energy (~50 eV) can penetrate film surface and make chemical bonds with carbon atoms. The peak energy in the C 1s spectra seems to shift close to sp^2 bonded carbon component for t_s > 2000 s. This shift may be explained by that sp^2 component selectively remained in the film.

The chemical composition of C, B, O and Si as a function of t_s was shown in Fig. 4. The boron concentration was ~55% in the vicinity of the film surface and decreased gradually with an increase of t_s.

4. Conclusion

Boron thin films were deposited on carbon films by PLD. AFM analysis showed that the domain size on the film surface increased after the boron was deposited. XPS analysis revealed that the double layer film contained chemical bond between carbon and boron atom. This result may indicate that, by depositing carbon and boron films alternatively, it is possible to prepare carbon thin film doped with required concentration of boron for an electron emission material.

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