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Boron and nitrogen co-doping of diamond-like carbon film for transparent conductive films

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ABSTRACT

We demonstrate boron and nitrogen co-doping of diamond-like carbon (DLC) film by vaporizing borane ammonia for applications in anti-scratch and extremely robust transparent conductive films. This method allows for facile fabrication of boron and nitrogen co-doped DLC (BNDLC) film with ultra-flat surface and uniform thickness. The simultaneous occurrence of graphitization and boron and nitrogen co-doping of DLC film induced by increasing the co-doping temperature was observed and lead to a significant decrease in the sheet resistance. As a result, the sheet resistance and optical transmittance at 550 nm of the BNDLC were $3.53 \pm 0.19 \text{ k}\Omega/\text{sq}$ and 81.25%, respectively.

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1. Introduction

Carbon is a unique element that has many allotropic forms: zero-dimensional fullerene, one-dimensional carbon nanotube, two-dimensional graphene, and three-dimensional graphite or diamond. These atomic bonding configurations are responsible for determining the electronic and physical properties. In particular, graphene has emerged as a promising material for flexible transparent electrodes for applications in foldable displays due to their remarkable electrical properties, high optical transmittance, and flexibility [1–5]. However, a reliable method for fabrication of anti-scratch and extremely robust flexible transparent films is needed to meet the demands of the target applications. Although diamond-like carbon (DLC) films possess strong hardness, superior anti-scratch property, low fractional coefficient, and high optical transmittance, they also have electrical insulation properties because of the coexistence of trigonal (sp²) and tetrahedral (sp³) bonded carbon matrices [6]. Hence, the improvement of electrical conductivity of DLC films is a prerequisite for realization of DLC-based flexible transparent electrodes. Previous reports have demonstrated that chemical doping using various dopants, such as B, N, Zn, P, I, Si, Co, and Mo, can lead to improved electrical conductivity [7-15].

Here, we present boron and nitrogen co-doping of DLC films to improve the electrical conductivity. The structural, chemical, and electrical properties of boron and nitrogen co-doped DLC (BNDLC) films formed by adjusting the co-doping temperature (T_{cd}) were systematically investigated. The sheet resistance and optical transmittance of the BNDLC films were examined for applications in transparent conductive films.

2. Experimental details

2.1. Deposition of diamond-like carbon (DLC) films

DLC films were deposited on Si(001) wafers or 100- μ m-thick Cu foil by hot filament plasma enhanced chemical vapor deposition (HF-PECVD). The substrates were located inside the chamber and heated to 200 °C under 7 × 10⁻⁷ Torr. Before DLC deposition, the substrates were pre-cleaned by Ar (22.5 sccm) plasma treatment at 150 W for 25 min under 1 × 10⁻⁴ Torr. After this pre-cleaning process, benzene (C₆H₆, 24 sccm) was introduced as a carbon feedstock for 5 and 55 min to deposit DLC.

2.2. Co-doping of diamond-like carbon (DLC) films using borane ammonia vaporization

The DLC films and borane ammonia (H_6NB , 0.05 g) on an alumina boat were placed in thermal CVD (TCVD). The distance between the DLC films and H_6NB was 15 cm. TCVD was heated at

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Fig. 1. (a) A photograph of Si and DLC coated on Si(001) substrates using HF-PECVD. (b) Optical microscope image (scale bar = 1 μ m) of DLC on Si. (c) Raman G-band intensity map (scale bar = 1 μ m) of DLC on Si (excitation wavelength: 532 nm). (d) Raman spectra of DLC on Si.

 T_{cd} = 300–1000 °C under 330 mTorr, and H₂ (20 sccm) was applied for 10 min for the B and N co-doping of DLC films.

3. Results and discussion

Fig. 1(a) is a photograph of Si(001) and DLC on Si(001), in which Si(001) substrate is blackened after DLC deposition. A typical optical microscope image and Raman G-band intensity map at \sim 1550 cm⁻¹ show that almost no color variation is observed, indicating defect-free DLC film with a uniform thickness, as shown in Figs. 1(b and c). The Raman spectrum of DLC film shows a broad peak around 1547 cm⁻¹, as shown in Fig. 1(d), identical to the results of a previous report [16].

Figs. 2(a and b) display atomic force microscopy (AFM; Seiko, SPM400) images ($1 \ \mu m \times 1 \ \mu m$) of DLC and BNDLC films prepared at T_{cd} = 900 °C by vaporizing H₆BN for 10 min with a flow of H₂. The root mean square (RMS) roughness obtained from DLC and BNDLC films were 0.38 and 0.49 nm, respectively, indicating films with an ultra-flat surface were formed. The thicknesses of DLC and BNDLC films were estimated to be 432 and 477 nm, respectively (Figs. 2(c and d)), which means that the thickness of the film increased slightly after doping. An amorphous capping layer with a thickness of ~8 nm was clearly observed after doping, as observed by high-magnified transmission electron microscopy (TEM; JEOL, JEM2100F) (Fig. 2(e and f)). From this observation, we anticipate that the co-doping of B and N may preferentially occur at the surfaces of DLC films.

The structural feature of the BNDLC film prepared by adjusting T_{cd} (300–900 °C) was examined by Raman spectroscopy (Renishaw, RM1000 inVia) with an excitation wavelength of 514 nm. Fig. 3(a)



Fig. 2. (a and b) AFM images, (c and d) low- (scale bar = 200 nm) and (e and f) highmagnification (scale bar = 100 nm) TEM images of DLC (left) and BNDLC (right) films on Si(001) substrates.

exhibits D- and G-bands spectra of the BNDLC films formed at various T_{cd} , in which the G-band experiences a significant blueshift and the intensity of the D-band increases gradually with increasing T_{cd} . The sheet resistances of the BNDLC films were measured by four-point probe technique, as shown in Fig. 3(b). There was an abrupt decrease in the sheet resistance between 300 and 600 °C, followed by a gradual decrease up to 900 °C (inset of Fig. 3(b)). These results could be responsible for the graphitization of the BNDLC at high temperature [17,18]. In addition, no noticeable changes in the Raman spectra were observed after adjusting H₂ flow rate at fixed T_{cd} (not shown here).

The chemical identification of the BNDLC films was performed by X-ray photoelectron spectroscopy (XPS; VGMICRO TECH, ESCA 2000). XPS spectra were acquired with normal emission geometry using conventional monochromatic Al K α radiation (hv = 1486.6 eV). Fig. 4(a) exhibits C1s core level spectra obtained from the BNDLC films prepared by adjusting T_{cd} . The C–B bond (binding energy $(E_B) = 282.8 \text{ eV}$), sp² C–C bond $(E_B = 283.8 \text{ eV})$, sp^3 C–C bond (E_B = 284.7 eV), and C–N bond (E_B = 285.3 eV) were assigned and coincide with the results of a previous report [19]. The intensity of the sp³ C–C bond decreased, whereas that of the sp^2 C–C bond increased with increasing T_{cd} . Also, the intensity of C–B bond at a lower $E_{\rm B}$ and C–N component at a higher $E_{\rm B}$ increased simultaneously with increasing T_{cd} , resulting in spectral broadening. This can be explained by the co-occurrence of graphitization and co-doping. Fig. 4(b and c) shows N1s and B1s core level spectra of the BNDLC films prepared by adjusting T_{cd} . These results reveal N-B, N-C, N-O, B-C, B-N, and B-O bonds at temperatures over 600 °C [19]. Fig. 4(d-g) exhibits XPS survey, C1s, N1s, and B1s spectra of the BNDLC formed at T_{cd} = 900 °C, respectively, indicating that Download English Version:

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