

Enhancement of electrical conductivity and electrochemical activity of hydrogenated amorphous carbon by incorporating boron atoms

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Abstract. Conductive boron-doped hydrogenated amorphous carbon (B-DLC) thin films were successfully synthesized with RF plasma-enhanced CVD method. By incorporating boron atoms in amorphous carbon, conduction types were changed from n- to p-type, and volume resistivity was decreased from 30.4 (non-doped) to $6.36 \times 10^{-2} \Omega \text{ cm}$ (B/C = 2.500 atom%). B-DLC film with $sp^2/(sp^2 + sp^3)$ carbons of 75 atom% exhibited high resistance to electrochemically-induced corrosion in strong acid solution. Furthermore, it was clarified that boron atoms in DLC could enhance kinetics of hydrogen evolution during water electrolysis at B-DLC surface. B-DLC is, therefore, a promising electrode material for hydrogen production by increasing the concentration of boron atoms in B-DLC and enhancing the reactivity of H_2 evolution.

1. Introduction

High stability for electrochemically-induced corrosion and availability at lower production costs are necessary for the electrode materials used in electrolytic industries that produce chemicals such as sodium hydroxide, hydrogen and chlorine, which are essential in industrialized world.

Incorporation of impurity atoms has been commonly used to enhance the conductivity of semiconductor. Our research group has developed conductive hydrogenated amorphous carbon thin films by incorporating nitrogen atoms (N-DLC) that could be synthesized at low cost^[1]. N-DLC films showed high chemical stability, and could be used as a polarizable electrode material in electroanalytical assay as well as boron-doped diamond electrodes. It, however, is necessary to reduce power loss resulting from electrode resistance and overpotential for hydrogen evolution in order to apply the film practically to electrolytic industries that produce pure material by passing larger current on electrodes.

N-DLC film contained a large number of nitrogen atoms ($> 8 \text{ atom\%}$, $7.0 \times 10^{21} \text{ cm}^{-3}$). Nevertheless, carrier density ($7.5 \times 10^{18} \text{ cm}^{-3}$) of N-DLC film was relatively lower than atom% of nitrogen atoms in DLC. Therefore, most of nitrogen atoms in DLC did not contribute to increase carrier density of n-type conduction. In this study, boron atoms were employed as impurity atoms. The conductivity of boron-doped hydrogenated amorphous carbon (B-DLC) is expected to be higher than that of N-DLC because boron atoms do not form multiple bonding with carbon atoms.



In this study, amorphous carbon electrodes with high conductivity and high chemical stability were fabricated by doping boron atoms and by controlling the amount of sp^2 bonded carbons. Moreover, the improvement of electrochemical activity of hydrogen evolution was attempted by controlling the concentration of boron atoms.

2. Experimental

B-DLC thin films were prepared using plasma-enhanced chemical vapor deposition (CVD) with RF-self bias system (model BP-10, SAMCO Co., Ltd.). Films were deposited on n-Si (111) substrates ($< 0.02 \Omega \text{ cm}$, SUMCO Co., Ltd.) after ultrasonic cleaning with 2-propanol for 15 minutes and in-situ sputter cleaning with argon plasma (200 W for 15 min.). Vapor at a flow rate of 5 mL min^{-1} was introduced into an evacuated reaction chamber from a degassed mixed solution of *n*-hexane and trimethyl borate ($\text{B}(\text{OCH}_3)_3$, TMOB) (carbon and boron sources) kept at room temperature. Argon was simultaneously introduced into the reaction chamber with a source gas. The atom% of boron in DLC was adjusted by the concentration of TMOB in *n*-hexane. B-DLC Films with a thickness of $0.68 \mu\text{m}$ were grown by applying RF power (350 W, 13.56 MHz) to cathode that held Si substrates on a quartz liner. The atom% of $sp^2/(sp^2 + sp^3)$ carbons in B-DLC was controlled by the temperature of a substrate during CVD synthesis. The temperature of the substrate used for films with sp^2 content of 82 % was set at $300 \text{ }^\circ\text{C}$, and for films with sp^2 content of 75 % was set at $275 \text{ }^\circ\text{C}$. The pressure in the reaction chamber was adjusted at 40 Pa. The deposition time was 40 minutes.

The resulting B-DLC films were characterized by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and Hall-effect measurement. The electrochemical measurements were carried out using B-DLC films (geometric area: 0.1 cm^2) as a working electrode, $\text{Ag}|\text{AgCl}$ electrode as a reference electrode, and Pt coiled wire as a counter electrode in a three-electrode cell.

3. Results and Discussion

3.1. Film Characterization

TMOB used as boron source is resistant to decomposition in partially-ionized plasma of CVD synthesis because B-O bonding with higher bond strength (5.4 eV, C-C; 3.6 eV) is included in TMOB molecule. To enhance TMOB decomposition by the collision with Ar^* metastable atoms and/or Ar^+ ions, argon gas was introduced in the reaction chamber during deposition^[2]. By adding Ar gas, conduction types in B-DLC were changed from n- to p-type. And then, higher values of carrier density and carrier mobility of B-DLC could be achieved than those of N-DLC as shown in **Table 1**.

The atomic concentration ratio of B-DLC was examined by XPS spectra. B 1s peak was clearly observed. The change of conduction type from n- to p-type shown in **Table 1** suggests that boron atoms are included in DLC and act as acceptors. The resistivity of B-DLC reached $6.36 \times 10^{-2} \Omega \text{ cm}$ (at 100 sccm of Ar flow rate). This value was more than 20 times lower than that of N-DLC. By

Table 1 Hall measurement results of non-doped DLC, B-DLC (B/C = 2.500 atom% in the source gas) and N-DLC

Sample	Ar flow rate (sccm)	Carrier density (10^{18} cm^{-3})	Mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	Resistivity ($\Omega \text{ cm}$)	Hall coefficient ($\text{cm}^3 \text{ C}^{-1}$)	Type
non-doped DLC	100	0.12	1.73	30.4	-52.57	n
B-DLC	0	2.93	3.60	5.93	-21.30	n
B-DLC	100	12.90	7.59	6.36×10^{-2}	+0.48	p
N-DLC	-	0.57	7.52	1.44	-10.85	n

using B-DLC films as electrode materials in electrolytic industries, power loss caused by electrode resistance can be reduced to one twenty-second. The concentration of impurity atoms (dopant atoms) in N-DLC films (8.0 atom%) is larger than that of B-DLC films (1.3 atom%). However, carrier density of N-DLC was lower than that of B-DLC. This lower carrier density resulted in the resistivity of N-DLC higher than that of B-DLC. The incorporation of boron atoms was found to be more efficient for enhancing conductivity than nitrogen atom incorporation. A similar result has been reported by C. Ronning *et al.* [3]. In order for impurity atoms in DLC to function as donors or acceptors, four single bonds with carbon atoms should be formed. The calculation results that boron atoms in amorphous carbon are preferentially bonded to sp^3 -bonded carbons have been reported [4]. On the other hand, it has been reported that nitrogen atoms are preferentially formed quite stable multiple bonding such as $=C=N-$ and $-C\equiv N$, which does not contribute to conductivities [5]. Consequently, boron atoms are more effective to increase carrier density than nitrogen atoms. The carrier density higher than that at N-DLC can be achieved at B-DLC although dopant concentration of B-DLC is lower than that of N-DLC.

3.2. Susceptibility to surface corrosion in strong acid media

To evaluate the inertness of B-DLC films toward electrochemically induced corrosion, the potential cycle treatment was carried out in 1.0 M HNO_3 + 0.1 M KF from -0.65 V to +1.3 V at 25°C for 2 hours [5]. **Fig. 1** shows optical micrographs of B-DLC and glassy carbon (GC) surfaces before and after potential cycling. At the surfaces of B-DLC with $sp^2/(sp^2 + sp^3)$ carbons of 82 atom% and GC, pits (30 – 100 μm in diameter) were formed (**Fig. 1-A** and **C**). The electrode surface corrosion might occur primarily by carbon gasification producing CO_2 and/or CO . On the contrary, B-DLC surfaces with $sp^2/(sp^2 + sp^3)$ below 75 atom% were identical after cycling (**Fig. 1-B**).

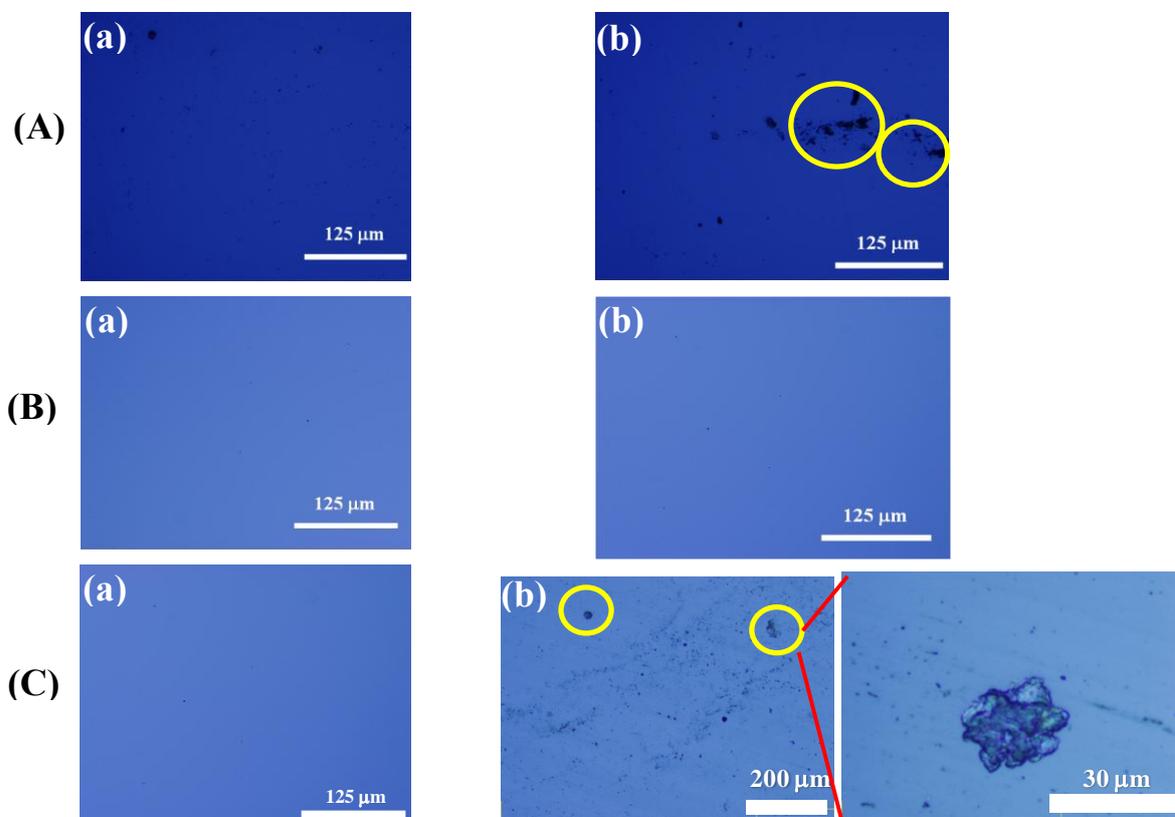


Fig. 1 Optical micrographs of (A) GC, (B) B-DLC (sp^2 ; 75 %) and (C) B-DLC (sp^2 ; 82 %) surfaces (a) before and (b) after potential cycling

B-DLC films with sp^2 of 75 atom% were fabricated under the following conditions; A temperature of substrate was set at 275 °C (< 275 °C). RF power of 350 W was applied. It has been known that sp^2 bonded carbon based electrodes show lower resistance to corrosion at anodic polarization than that of electrode materials including sp^3 bonded carbon [6]. In DLC films with sp^2 -bonded carbons of 50 atom% ($sp^2:sp^3 = 1:1$), which were uniformly distributed, sp^2 clusters are thought to be not formed because all carbon forms sp^2 - sp^3 bonding. In DLC films with sp^2 of 75 atom%, excess sp^2 -bonded carbons might form sp^2 - sp^2 bondings. As a result, sp^2 cluster (sp^2 - sp^2 - sp^2) is formed. The resistance to corrosion at DLC was lower with higher (> 75 atom%) sp^2 -bonded carbons. B-DLC electrode with much higher resistance to electrochemically-induced corrosion could be fabricated by decreasing the amount of sp^2 -bonded carbons. From these results, it can be concluded that highly conductive B-DLC film fabricated in this study can be applied as an electrode material with reliability in long-term electrochemical use.

3.3. Electrochemical Characterization

Fig. 2 shows the cyclic voltammograms for B-DLC electrode in 0.1 M H_2SO_4 . The onset potential for hydrogen evolution (at which current densities reached -0.2 mA cm^{-2}) was positively shifted from -1.61 to -1.41 V vs. Ag|AgCl when boron concentration in the source gas was increased from 0.625 to 2.500 atom% during B-DLC synthesis. The overpotential for hydrogen evolution was decreased by approximately 200 mV. The overpotential for oxygen evolution was not changed (slightly decreased by 30 mV). The amount of boron atoms in DLC may strongly affect the rate of hydrogen evolution.

In order to clarify the dependence of the parameter of the rate of hydrogen and oxygen evolution on the concentration of boron atoms in DLC, values of exchange current density i_0 and transfer coefficient α were estimated from Tafel plot (**Fig. 3**). The values are summarized in **Table 2**. The exchange current density i_0 is the value proportional to standard rate constant k_0 and the transfer coefficient α is a measure of the energy barrier. **Fig. 3** shows Tafel plots of B-DLC synthesized under various boron concentrations in 1.0 M H_2SO_4 .

For oxygen evolution, the values of transfer coefficient α stayed constant for all boron concentration in the source gas. The value of exchange current density i_0 was slightly increased with increasing boron concentration. These results indicate that boron concentration is indifferent to the kinetics of oxygen evolution. In contrast, for hydrogen evolution, the values of transfer coefficient α were not changed (0.18 ~ 0.14) and the values of exchange current density i_0 were increased by one order of magnitude (from 1.47×10^{-8} to $3.70 \times 10^{-7} \text{ A cm}^{-2}$) with increasing boron concentration from 0.625 to 2.500 atom%. The kinetics of hydrogen evolution was drastically enhanced with boron atoms in DLC films.

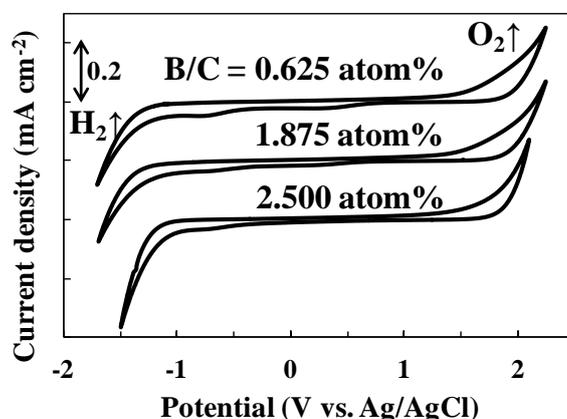


Fig. 2 Cyclic voltammograms in 0.1M H_2SO_4 at B-DLC electrodes deposited under various boron concentrations in the source gas. Sweep rate, 100 mV s^{-1} .

Table 2 The values of i_0 and α for hydrogen and oxygen evolution at B-DLC electrodes.

B/C ratio (atom %)	H ₂ evolution			O ₂ evolution		
	i_0 (10 ⁻⁸ A cm ⁻²)	slope ⁻¹ (mV dec ⁻¹)	α	i_0 (10 ⁻⁶ A cm ⁻²)	slope ⁻¹ (mV dec ⁻¹)	α
0.625	1.47	336	0.18	2.63	415	0.14
1.875	2.14	339	0.17	3.53	405	0.15
2.500	37.0	413	0.14	5.08	418	0.14

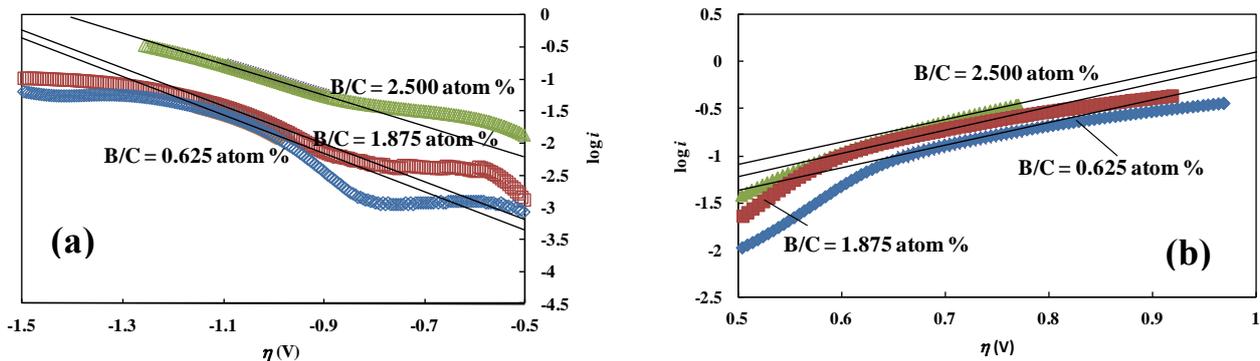


Fig. 3 Tafel plots in the potential region for (a) hydrogen evolution and (b) oxygen evolution at B-DLC electrodes. Electrolyte, 1.0 M H₂SO₄. Sweep rate, 50 mV min⁻¹.

These results indicate that the shape of potential curve of H₂ evolution was not changed but the activation energy was decreased with boron concentration. It suggests that boron atoms in DLC may act as an electrochemical catalyst for H₂ evolution. Thus, the electrochemical reactivity for hydrogen evolution at B-DLC surface could be enhanced by increasing boron concentration.

Fig. 4 shows cyclic voltammograms for B-DLC and N-DLC electrodes in 0.1 M H₂SO₄. The overpotential for hydrogen evolution at B-DLC with B/C = 2.500 atom% was lower than that at N-DLC by ca. 400 mV. The loss of electric power for H₂ production by water electrolysis could be decreased by using B-DLC electrode. However, the overpotential for hydrogen evolution at B-DLC surface is extremely higher than that at metal electrodes such as Pt. B-DLC can be applied as electrode materials with high corrosion resistance in electrolytic industries by increasing the concentration of boron atoms in DLC and enhancing the electrochemical reactivity for H₂ evolution.

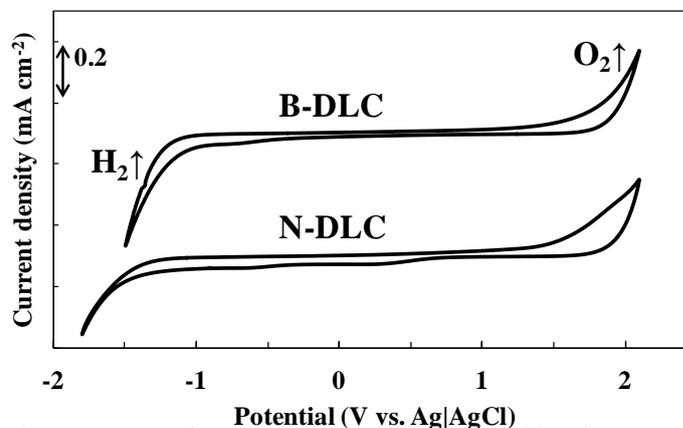


Fig. 4 Cyclic voltammograms in 0.1M H₂SO₄ at B-DLC with B/C = 2.500 atom% and N-DLC electrodes. Sweep rate, 100 mV s⁻¹

4. Summary

B-DLC films with lower resistivity than that of N-DLC films could be fabricated by incorporating boron atoms as a dopant. Boron concentration and volume resistivity of B-DLC synthesized at B/C = 2.500 atom% in the source gas were 1.3 atom% and $6.36 \times 10^{-2} \Omega \text{ cm}$, respectively. The electric power loss resulting from electrode resistance of B-DLC was lower than that of N-DLC because the volume resistivity of B-DLC was 22 times lower than that of N-DLC.

B-DLC films with sp^2 -bonded carbon of 75 atom% could be fabricated under the following deposition condition; A temperature of the substrate was $< 275 \text{ }^\circ\text{C}$ and RF power was $< 350 \text{ W}$. B-DLC films with sp^2 of 75 atom% show a high resistance to electrochemically-induced corrosion in strong acid solution in long-term electrochemical use.

The electrochemical reactivity of hydrogen evolution could be improved by increasing the concentration of boron atoms in DLC. Hence, the loss of electric power derived from the overpotential for hydrogen evolution at B-DLC was lower than that of N-DLC.

B-DLC is promising electrode material with higher reliability in long-term use and lower electric power loss in hydrogen production by water electrolysis.

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