

Conductive Diamond-like Carbon Film Deposition by Low Temperature Neutral Beam Enhanced Chemical Vapor Deposition for Bio-LSIs

Xijiang Chang¹, Yoshiyuki Kikuchi^{1,2}, Tomohiro Kubota¹, Kumi. Y. Inoue³,
Tomokazu Matsue^{3,4} and Seiji Samukawa^{1,4}

¹ Institute of Fluid Science, Tohoku University

2-1-1 Katahira, Aoba-ku, Sendai, 980-8577, Japan

Phone: +81-22-217-5240; E-mail: samukawa@ifs.tohoku.ac.jp

² Tokyo Electron Limited, Technology Center Sendai

2-1 Osawa 3-chome, Izumi-ku, Sendai, 981-3137, Japan

³ Graduate School of Environmental Studies, Tohoku University

6-6-11-604 Aramaki-aza-Aoba, Aoba-ku Sendai, 980-8579, Japan

⁴ WPI-Advanced Institute for Materials Research, Tohoku University

2-1-1 Katahira, Aoba-ku, Sendai, 980-8577, Japan

Abstract

Diamond-like carbon (DLC) film has good chemical stability and mechanical properties, so it is expected to be applicable in many applications such as electronic, mechanical, and biomedical. We fabricated conductive DLC film by using the neutral beam enhanced chemical vapor deposition technique at low temperature. Toluene was used as a precursor excited by Ar neutral beam to form a large conjugated system in the DLC film. Nitrogen doping was used to increase film conductivity. The conductive DLC film functioned as an electrode in solution and exhibited good electrochemical properties. Such DLC film is expected for use as the electrode material in bio-LSIs to provide better bio-sensing sensitivity and wider operation potential range.

1. Introduction

Diamond-like carbon (DLC) is amorphous carbon containing both diamond bonding (sp^3) and graphite bonding (sp^2), so it maintains good mechanical properties similar to diamonds and it may also exhibit some electrical properties due to the graphite structure [1, 2]. It also exhibits good chemical stability and biocompatibility. With these advantages, the DLC film is a powerful candidate as a bio electrode material [3]. Recently, bio-LSIs have been developed as advanced bio-sensing devices for electrochemical bio-imaging [4]. In this application, conductive DLC electrodes are expected to provide a more sensitive bio-imaging platform for a wide range of applications compared to Pt electrodes. To apply DLC film for this use, the challenge is to carry out conductive DLC deposition at low temperature because the integrated transistors in bio-LSIs cannot be processed at high temperature. In this study, we conducted DLC film deposition at room temperature with the neutral beam enhanced chemical vapor deposition (NBECVD) technique. Compared to the traditional CVD technique, the NBECVD technique has an advantage in that there is no damage from UV and charge particles on the target [5]. The neutral beam energy can be

precisely controlled for proper precursor dissociation, which is beneficial for controlling film structure in deposition.

2. Experiment

We used the NBECVD system [5] shown in Fig. 1. The neutral beam generator is based on a large radius surface-wave plasma generator driven by 2.45 GHz microwave. The carbon aperture is set in the chamber, separating it into plasma and deposition chambers. The carbon aperture can neutralize the ions in the plasma to form a neutral beam in the deposition region. The aperture also blocks UV and electrons. A 150-kHz RF source is used to add bias on the aperture, which can adjust the neutral beam energy by accelerating the ions in the plasma. In the CVD process, precursor gas is injected into the deposition chamber and irradiated by the neutral beam.

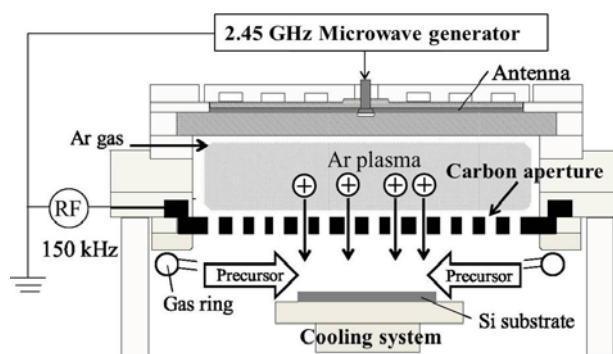


Fig. 1 Schematic of NBECVD system

We selected toluene as the precursor, which is thought to become excited to form a polycyclic aromatic hydrocarbon structure, as shown in Fig. 2.

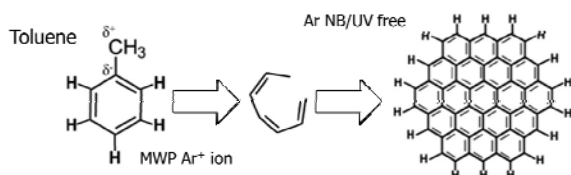


Fig. 2 Schematic of polycyclic aromatic hydrocarbon structure growth from excited toluene

The DLC film is deposited on 8-inch Si wafer on the stage, to which the cooling system is connected to sustain a temperature of -50°C . In the deposition process, the wafer temperature can be limited to below 20°C , so the deposition can be considered as at room temperature. We use Ar as the plasma gas and the microwave power is 3.25 kW. The RF bias added to the aperture is about 150 W to sustain proper Ar neutral beam energy. To increase film conductivity, N_2 and H_2 are added for nitrogen doping [6, 7]. For the purpose to be used as electrode material, deposition is also done on a Si wafer with 100 nm of sputtered Pt.

3. Results and discussion

The DLC film thickness was measured using an ellipsometer. The thickness of the Si substrate was around 120 nm after 30-min deposition. Sheet resistivity was measured using a 4-probe system. With optimized pressure and bias conditions, film conductivity reached 10^3 S/m . Nitrogen doping was used to increase film conductivity. The chamber was filled with N_2 and H_2 mixture gas with a ratio of 4:1 is as the nitrogen source. After doping deposition, film conductivity was measured. The value increased 2 orders in magnitude compared to the non-doped film. X-ray photoelectron spectroscopy was applied on the film, and obvious N 1s peak was detected.

For use as electrodes, the DLC adhesion to metals was evaluated. Platinum was selected as the substrate metal due to its good adhesion. The DLC film was deposited on an 8-inch Si wafer with a 100-nm sputtered Pt layer. The electrochemical property was characterized using the cyclic voltammetry method. The electrode area was circular and 2 mm in diameter, shaped using Elegrip tape. The electrode sample was put into a 2.0 mM ferrocenemethanol solution with 0.1 M KCl and scanned in the range from -0.6 to 0.8 V with a scan rate of 100 mV/s . The results are shown in Fig. 3 (a). Redox peaks of ferric ions were detected. In Fig. 3 (b) the potential window of the DLC film was measured with $0.5 \text{ mM H}_2\text{SO}_4$ solution. Compared to Au and Pt electrodes, the conductive DLC electrode had a wider potential window, which is similar to graphite at high-temperature annealing at 600°C . With such electrochemical properties, the conductive DLC film can be used on bio-LSIs instead of Pt electrodes. This work is still in progress and the challenge is the deposition uniformity on the electrode arrays of bio-LSI chips.

4. Conclusions

We fabricated conductive DLC film by using the NBECVD technique at low temperature. Neutral beam energy can be controlled to properly dissociate the Toluene to form a conductive conjugated structure in the film. Nitrogen doping can significantly help increase film conductivity. The conductive DLC film worked as an electrode in solution and exhibited good electrochemical properties. In potential window testing, the DLC film showed a wider potential window than common metal electrodes such as Pt and Au. This conductive DLC film is expected for use as the electrode material in bio-LSIs to provide better imaging performance.

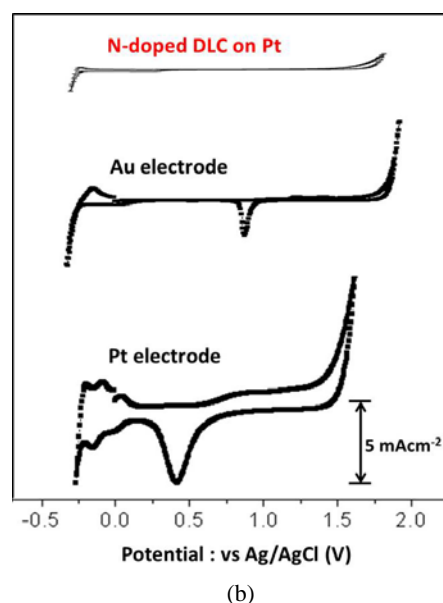
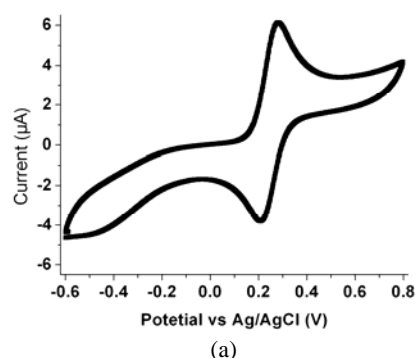


Fig. 3 Cyclic voltammograms of N-doped DLC film: (a) in 2.0 mM ferrocenemethanol solution with 0.1 M KCl; (b) in 0.5 mM H_2SO_4 solution

References

- [1] J. Robertsom. *Mater. Sci. Eng., R* **37** (2002) 129-281.
- [2] Y. Lifshitz. *Diamond Rel. Mater.* **5** (1996) 388.
- [3] R. L. McCreery. *Chem. Rev.* **108** 2008 2646-2687.
- [4] K. Y. Inoue, *et al.* *Lab Chip.* **12** (2012) 3481-90.
- [5] Y. Kikuchi, *et al.* *Carbon* **67** (2014) 635-642.
- [6] Y. An, *et al.* *Phys. Chem. Chem. Phys.* **14** (2012) 15802-6
- [7] D. Jana, *et al.* *Prog. Mater. Sci.* **58** (2013) 565-635