



# Impacts of substrate bias and dilution gas on the properties of Si-incorporated diamond-like carbon films by plasma deposition using organosilane as a Si source

H. Nakazawa\*, S. Miura, K. Nakamura, Y. Nara

Graduate School of Science and Technology, Hirosaki University, 3 Bunkyo, Hirosaki, Aomori 036-8561, Japan

## ARTICLE INFO

### Keywords:

Diamond-like carbon  
Silicon  
Chemical vapor deposition  
Internal stress  
Adhesion  
Tribology

## ABSTRACT

We have deposited silicon-incorporated diamond-like carbon (Si-DLC) films by plasma-enhanced chemical vapor deposition using monomethylsilane ( $\text{CH}_3\text{SiH}_3$ ; MMS) as a Si source, and systematically investigated the impacts of substrate bias and dilution gas on the mechanical and tribological properties of the Si-DLC films. The use of a pulse bias and hydrogen dilution is very effective in suppressing the generation of particles during the deposition. The internal stress of the Si-DLC films deposited using the pulse bias tended to be lower than that of the Si-DLC films deposited using a DC bias, while the hydrogen dilution resulted in the increase in the internal stress. On the other hand, the Si-DLC film deposited with  $\text{H}_2$  using the pulse bias showed the highest adhesion strength and the lowest friction coefficient. The use of the pulse bias resulted in the increase in the wear resistance.

## 1. Introduction

Diamond-like carbon (DLC) films have attracted much attention because they have excellent properties such as high hardness, low friction, high wear resistance, high electrical resistivity, high optical transparency, low gas permittivity, high biocompatibility. Therefore, DLC films have been used in a wide range of industrial applications such as coatings on magnetic storage disks, cutting tools, PET bottles, mechanical parts, molds, optical lenses [1–10]. They are also of significant interest as semiconductor materials for solar cells, interlayer dielectric materials for semiconductor integrated circuits, micro-actuator materials for micro-electromechanical systems, and biocompatible materials for implants and medical devices in contact with blood [11–16].

One of the issues for these applications is that there commonly exist high internal stresses in DLC films. The high internal stresses cause the delamination of the DLC films or the deformation of the substrates. The addition of hetero elements to DLC films is one of the effective solutions to decrease the internal stress. In particular, the addition of silicon (Si) into DLC films has been intensively studied because of the reduction of the internal stress and the improvements in the thermal stability and the friction performance under air atmosphere and aqueous and cor-

rosive solution conditions [17–23]. However, it has a drawback that the Si addition reduces the wear protection and hardness of the DLC films [24–27]. Besides, particles composed chiefly of Si were generated during plasma deposition [28].

Pulsed substrate bias has been employed to improve the mechanical and tribological properties of DLC films prepared by plasma-enhanced chemical vapor deposition (PECVD) [21,29–31]. We demonstrated that the tribological properties of Si-DLC films deposited by PECVD using a pulse bias with Ar as a dilution gas were superior to those of Si-DLC films deposited using a DC bias with Ar [31]. In addition, the generation of particles on the Si-DLC films was markedly suppressed in the case of employing the pulse bias [31].

On the other hand, it has been reported that the use of hydrogen gas during plasma deposition leads to the improvement of the properties of DLC films [32–34]. We prepared silicon/nitrogen-incorporated DLC films (Si-N-DLC) by PECVD using a DC bias and found that the use of  $\text{H}_2$  as a dilution gas improved the adhesion strength and tribological properties of the Si-N-DLC films [34]. Furthermore, we compared the properties of hydrogen-free Si-DLC films prepared by pulsed laser deposition (PLD) with those of hydrogenated Si-DLC films by PLD with  $\text{H}_2$  and demonstrated that the hydrogenated Si-DLC films exhibited better

\* Corresponding author.

E-mail address: [hnaka@hirosaki-u.ac.jp](mailto:hnaka@hirosaki-u.ac.jp) (H. Nakazawa).

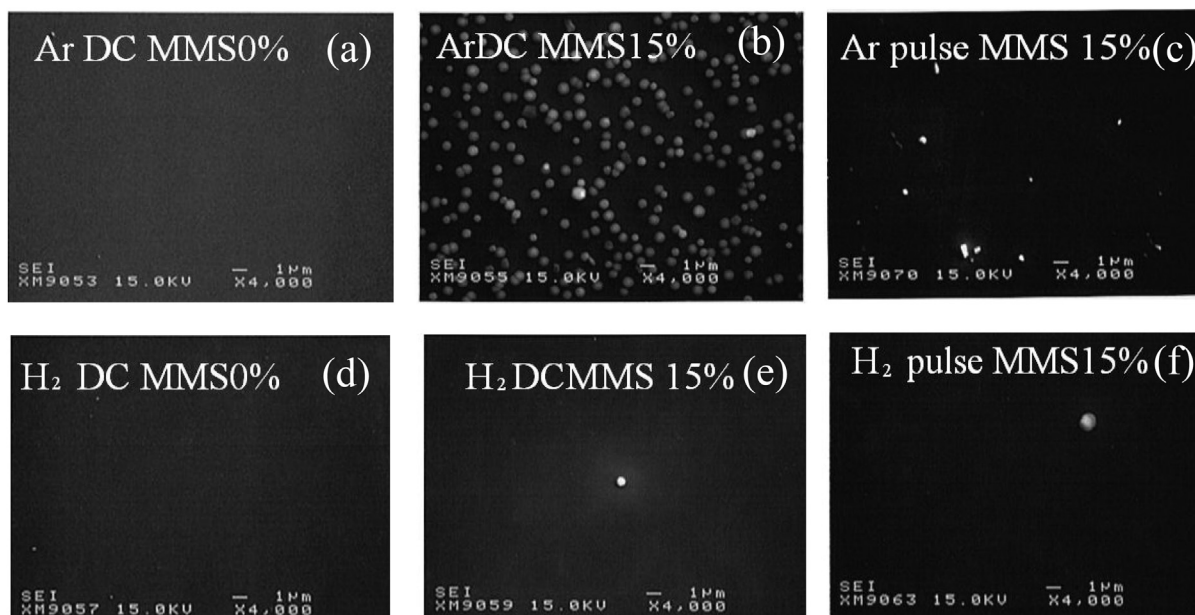


Fig. 1. SEM images of DLC films deposited at MMS flow ratios of (a,d) 0% and (b,c,e,f) 15% using (a,b,d,e) DC and (c,f) pulse biases. The films were deposited using (a,b,c) Ar and (d,e,f) H<sub>2</sub> as a dilution gas.

tribological properties than the hydrogen-free DLC films [27]. In spite of the significant works, the properties of Si-DLC films prepared by PECVD using a pulse bias with H<sub>2</sub> as a dilution gas have not been reported yet.

In this study, we have deposited Si-DLC films by plasma-enhanced chemical vapor deposition (PECVD) using monomethylsilane (CH<sub>3</sub>SiH<sub>3</sub>; MMS) as a Si source, and systematically investigated the impacts of substrate bias and dilution gas on the mechanical and tribological properties of the Si-DLC films. During the deposition, a negative pulse bias or a DC bias was applied to the substrate, and H<sub>2</sub> or Ar was used as a dilution gas.

## 2. Experimental

DLC films were prepared by radio-frequency CVD (RF-PECVD). The base pressure of the PECVD chamber was  $4.0 \times 10^{-5}$  Pa. The reactor was composed of two electrodes. RF power (13.56 MHz) was capacitively coupled to one of the electrodes. The plasma was excited by the RF field. The substrate used was a p-type Si(001) wafer. The substrate was rinsed with ethanol, acetone, and ethanol in an ultrasonic container, and it was mounted on the other electrode in the PECVD chamber. Prior to the deposition, the substrate surface was cleaned by Ar<sup>+</sup> etching in an Ar (> 99.999%) discharge. The sputtering conditions were described in our previous report [28]. The deposition of DLC films was carried out at an RF power of 40 W and a total pressure of 0.3 Pa. Total flow rate was kept at 44 sccm, and Ar or H<sub>2</sub> (> 99.99999%) gas was introduced into the chamber at a flow rate of 22 sccm. MMS (99.99%) flow ratio {MMS/[MMS + CH<sub>4</sub>(99.9999%)]} was changed from 0% to 15%. A negative DC or pulse bias was applied to the substrate during the deposition. The pulse bias has an effect on suppressing the continuous elevation of the surface temperature. The conversion of sp<sup>3</sup>-hybridized C to sp<sup>2</sup>-hybridized C is accelerated at high temperatures, leading to a loss of sp<sup>3</sup> bonding and a loss of diamond-like

properties. The voltage of the DC bias was −500 V. The peak voltage, duty ratio, and frequency of the pulse bias were −500 V, 25%, and 20 kHz, respectively.

The surface morphology of the DLC films was observed using a scanning electron microscope (JEOL JXA8340). The thickness of the DLC films was determined from the profilometric measurement of a step formed during the deposition using laser scanning microscopy (Olympus LEXTOLS4000). The deposition rate was calculated by dividing the thickness by the deposition time. The composition of the DLC films was measured by electron probe microanalysis (EPMA; JOEL JXA-8230RL). The chemical bonding of the films was characterized by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). XPS spectra were obtained using a Shimadzu ESCA1000 system with a Mg Kα X-ray tube and a hemispherical electron analyzer. FTIR spectra with a resolution of 4 cm<sup>−1</sup> were obtained using a JASCO FTIR6100 system. A beam-bending method was used to estimate the internal stress of the films. The structure of the films was characterized by visible Raman spectroscopy. Raman spectra with a resolution of 4 cm<sup>−1</sup> were obtained in a backscattering arrangement for 514.5 nm light from an Ar<sup>+</sup> laser (Renishaw RM2000).

The internal stress of the films was estimated by a beam-bending method using a thin Si(100) wafer as a substrate, whose thickness was ~400 µm. The deformation of the substrate due to the stress was measured by laser scanning microscopy (Olympus LEXTOLS4000). The internal stress was calculated from the radius of curvature of the beam using Stoney's equation [35]. The adhesion strength of the films was evaluated using a scratch tester (Rhesca CSR2000) using a diamond stylus. The radius of curvature of the stylus was 15 µm. The critical load was defined as the normal load required to peel off the films. The scratch furrow morphology of the films was observed using an optical microscope to find the peeling of the films. The scratch speed and loading rate were 10 mm/s and 2.5 mN/s, respectively. The tribological properties were examined by ball-on-plate reciprocating friction test

Download English Version:

<https://daneshyari.com/en/article/8032673>

Download Persian Version:

<https://daneshyari.com/article/8032673>

[Daneshyari.com](https://daneshyari.com)