Diamond & Related Materials 80 (2017) 38–44

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Structure and electrical properties of molybdenum-containing diamond-like carbon coatings for use as fatigue sensors

Hiroyuki Kosukegawa[a,*], Sophia Berkani[a], Hiroyuki Miki[b], Toshiyuki Takagi[a]

[a] Institute of Fluid Science, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan
[b] Frontier Research Institute for Interdisciplinary Sciences, Tohoku University, 6-3 Aramaki-aza, Aoba, Aoba-ku, Sendai, Miyagi 980-8578, Japan

ARTICLE INFO

Keywords:
Diamond-like carbon
Nanostructures
Electrical properties characterization
Sensors

ABSTRACT

Electrically conductive diamond-like carbon coatings containing metal grains (Me-DLC) have recently been suggested for use in sensors. We found that the electrical resistance of molybdenum-containing DLC (Mo-DLC) varies with increasing cycles of cyclic bending. Because of this aging property, Mo-DLC has potential as a fatigue sensor. In this paper, we analyzed the variation of nanoscopic structure of Mo-DLC by various spectroscopic techniques and clarified the mechanism underpinning the variation of the electrical properties of Mo-DLC in terms of the hopping conduction in Me-DLC. In the Raman spectra, the intensity ratio between the D-band and G-band of Mo-DLC gradually decreased with bending, which means that the sp^2 carbon in aromatic rings decreases in number. XPS indicates that carbide bonding (C–Mo) increased after bending for 10^7 cycles. Furthermore, EELS showed a decrease in π^* bonding in the a-C:H matrix with increasing cyclic bending. From these results, we assume a mechanism that the bonding condition of carbon in the matrix changes from sp^2 to carbide because the repeated bending stress changed the electrical properties of Mo-DLC. This knowledge can be useful for controlling the electrical and mechanical properties of Mo-DLC for sensing application. Furthermore, the characteristics of Mo-DLC, such as the variation in electrical properties, can be applied to sense fatigue in severe environments.

1. Introduction

Proactive preventative maintenance is best for infrastructure with long service time such as bridges, power plants, and tunnels [1]. It is better to detect potential defects or causes for defects before degradation begins, and various sensors have recently been used to sense the signs of defects. For instance, fatigue sensors can predict the residual life of structural materials used in huge, complex systems such as power plants. Fatigue sensors using various approaches have been proposed [2], some of which have already been commercialized. However, these sensors, all based on metallic materials, cannot tolerate extreme conditions such as corrosive environments. Therefore, a chemical-resistant fatigue sensor must be developed for use in corrosive environments.

Recently, we developed strain sensors with a metal-containing diamond-like carbon (Me-DLC) coating, and these sensors have demonstrated high chemical resistance and good shape deformation response [3–12]. We have also found that tungsten-containing DLC (W-DLC) exhibits good sensitivity as a commercial strain sensor [9,10]. The sensitivity of a sensor is sometimes evaluated using the gauge factor K. According to Grimaldi, the K of a nanocomposite in which metal grains are dispersed in an insulator matrix, such as Me-DLC, is described by

$$K = \frac{2d}{\xi}\frac{1 + 2r/d}{1 + (2r/d)(E_0/E_1)} \quad (1)$$

where d is the distance between metal grains, r is the radius of a metal grain, ξ is the localization length, and E_1 and E_0 are the Young's moduli of the metal and insulating matrix, respectively [13]. Based on Eq. (1), a nanocomposite dispersed in a metal with higher Young's modulus will exhibit a larger gauge factor. This relationship supports the concept that W-DLC [4–5,9–10] and molybdenum-containing DLC (Mo-DLC) [2,11,14] have electrical properties suited for sensing because W and Mo have good mechanical properties; the Young's moduli of W and Mo are 350 GPa and 325 GPa, respectively, which are much higher than those of other metals.

In addition, Bertran [15] and Ji [16] investigated the internal stress and adhesive strength of a DLC including W or Mo in multilayer structures and nanocomposites. A DLC including W or Mo has lower internal stress than an amorphous carbon film. These characteristics enable the DLC to be thicker and improve its adherence to the substrate. Ji [16] also showed that dispersing Mo nanograins in an a-C:H matrix

* Corresponding author.
E-mail address: kosukegawa@wert.ifs.tohoku.ac.jp (H. Kosukegawa).

http://dx.doi.org/10.1016/j.diamond.2017.09.018
Received 30 June 2017; Received in revised form 5 September 2017; Accepted 26 September 2017
Available online 28 September 2017
0925-9635/

greatly decreases the internal stress of the DLC. These reports indicate that a Mo-DLC coating may be a good chemical-resistant sensor.

In this study, we use Mo-DLC to make a corrosion-resistant fatigue sensor and investigate its sensitivity to changing fatigue caused by loading with cyclic bending. We discuss the relationship between electrical properties and its structure, based on alternative current impedance testing, morphological observation, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and electron energy-loss spectroscopy (EELS).

2. Materials and methods

2.1. Deposition of molybdenum-containing diamond-like carbon

We used a commercial elastic ceramic plate (Ceraflex®-A, Japan Fine Ceramics Co., Ltd.), with dimensions of 7.0 × 4.0 × 0.1 mm, as the substrate. This ceramic plate, made of zirconia, has high volume resistivity (10^{12} Ω·cm) and sufficient flexural strength (1200 MPa) to tolerate cyclic bending testing with a maximum bending strain of 500 με.

We prepared two types of DLC films: Mo-DLC and a-C:H (DLC without metal grains). The Mo-DLC film was deposited with a hybrid technique that combines plasma-enhanced chemical vapor deposition (PECVD) and DC magnetron sputtering, as shown in Fig. 1. The PECVD apparatus generates a capacitively coupled plasma by using a RF power source at 13.56 MHz. The self-bias voltage of the RF electrode was − 400 V, controlled with a capacitance-matching box. Methane (CH_4) gas—the carbon source for PECVD—and Ar gas used for sputtering were flowed into the reaction chamber. The flow rate of Ar gas was 7.5 sccm, maintained with mass flow controllers. The flow rate of CH_4 gas was controlled at 6.0 sccm. The Mo-DLC specimen is named “MoD”. Mo-DLC was produced by DC sputtering of a molybdenum target (Purity: 3 N7, ϕ101.6 × t5 (mm), Kojundo Chemical Laboratory Co., Ltd.) simultaneously with the PECVD. The DC sputtering power was 200 W. All specimens were prepared at a pressure of 1.3 Pa for 20 min.

The a-C:H film was prepared as a control by using PECVD only with CH_4 gas. The flow rate of CH_4 was maintained at 5.0 sccm, and the pressure of the process gas was 13 Pa. The processing time was 30 min. The self-bias voltage was − 600 V. The a-C:H specimen is named “C-DLC.”

The thicknesses of the MoD and C-DLC films were measured with a profilometer. The thicknesses of the MoD and C-DLC were 592 nm and 642 nm, respectively. The Mo atomic content was measured by energy-dispersive X-ray spectroscopy (EDX; UltraDry, Thermo Fisher Scientific Inc.) installed in a scanning electron microscope (SEM; JSM6510, JEOL Ltd.) operated at an acceleration voltage of 14 kV, spot size of 60, magnitude of 1000, working distance of 17 mm, and tilt angle of 30°. Table 1 shows the characteristics of the respective specimen.

Table 1
Deposition conditions and characteristics of the DLC coatings.

Specimen	Ar (sccm)	CH_4 (sccm)	Process time (min)	Thickness (nm)	Mo content (at.%)
MoD	7.5	6.0	20	592	35.5
C-DLC	0.0	5.0	12	642	0.0

2.2. Cyclic bending test and measurement of electrical resistance of DLC

After deposition, MoD was partly masked and dry-etched with Ar gas, and then shaped to dimensions of 7 × 0.75 mm^2. To measure the electrical resistance of Mo-DLC using the four-terminal method, four Cu terminals were deposited on the Mo-DLC film by DC sputtering, as shown in Fig. 2(a). The gap between each Cu terminal was 1.5 mm, and the width of the Cu electrode was 0.75 mm. Fig. 2(b) shows a typical specimen of MoD.

A carbon steel (AISI 1045) beam with dimensions of 10 × 150 × 1 mm^3 was used as the cantilever, which was fixed to the stage with a rear end margin of 50 mm for clamping. Mo-DLC and a-C:H specimens were glued, using cyanoacrylate adhesive agent, 10 mm away from the fixed end of the beam. The distance between the fixed end and the free end of the beam was 100 mm. The beam was vibrated at the resonance frequency by using an electromagnetic coil, as shown in Fig. 3(a) and (b). The resonance frequency f_n of a carbon steel cantilever beam with a free end is calculated from Eq. (2):

$$f_n = \frac{1}{2\pi}\frac{\lambda_n^2}{L^2}\sqrt{\frac{EI}{\rho A}} \tag{2}$$

where λ_n is a dimensionless constant that is equal to 1.875 for the primary mode of the natural frequency, L is the length of the beam, E is Young's modulus, I is the moment of inertia of area, ρ is the density, and A is the cross-sectional area. When the width of the beam is b and the height of the beam is h, I and A are calculated by $I = bh^3/12$ and

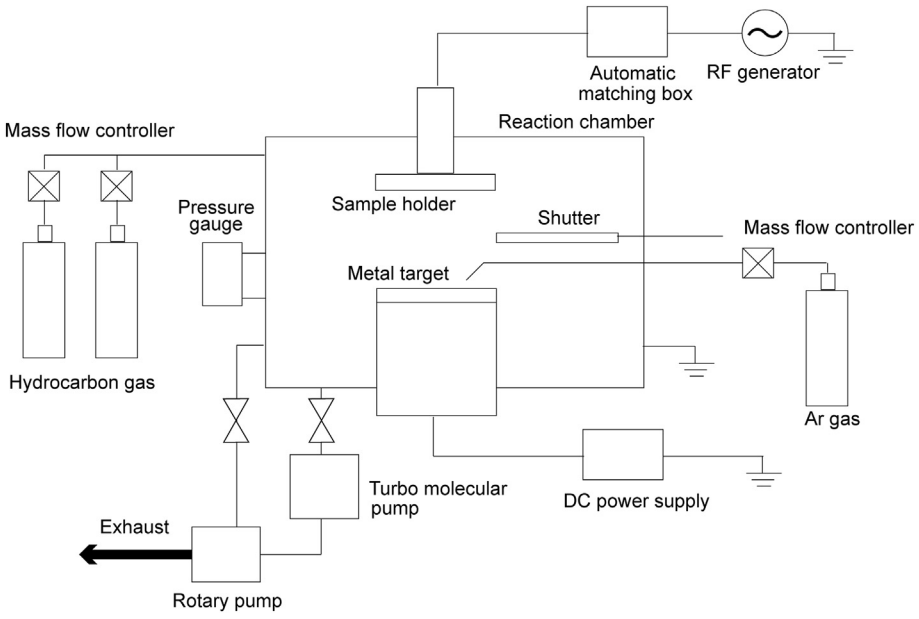

Fig. 1. Schematic of the hybrid deposition system for Mo-DLC and C-DLC.