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Effects of hydrogen and oxygen on the electrochemical corrosion and wear-corrosion behavior of diamond films deposited by hot filament chemical vapor deposition

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Abstract

A diamond film was deposited on silicon substrate using hot filament chemical vapor deposition (HFCVD), and H_2 and O_2 gases were added to the deposition process for comparison. This work evaluates how adding H_2 and O_2 affects the corrosion and wear-corrosion resistance characteristics of diamond films deposited on silicon substrate. The type of atomic bonding, structure, and surface morphologies of various diamond films were analyzed by Raman spectrometry, X-ray diffraction (XRD) and atomic force microscopy (AFM). Additionally, the mechanical characteristics of diamond films were studied using a precision nano-indentation test instrument. The corrosion and wear-corrosion resistance of diamond films were studied in 1 M H_2SO_4 + 1 M NaCl solution by electrochemical polarization. The experimental results show that the diamond film with added H_2 had a denser surface and a more obvious diamond phase with sp^3 bonding than the as-deposited HFCVD diamond film, effectively increasing the hardness, improving the surface structure and thereby improving corrosion and wear-corrosion resistance properties. However, the diamond film with added O_2 had more sp^2 and fewer sp^3 bonds than the as-deposited HFCVD diamond film, corresponding to reduced corrosion and wear-corrosion resistance.

Keywords: Diamond film; HFCVD; Wear-corrosion; Electrochemical corrosion

1. Introduction

Diamond films have many exceptional properties such as a large band gap, a high breakdown field, very high carrier mobilities [1]. Therefore, diamond films have potential for use in field emission displays (FED) [2,3]. They have excellent hardness and thermal conductivity, low friction coefficient, good chemical inertness and broad-band transparency from near-UV to far IR. These properties are such that diamond films have a wide range of applications in electronics, optics, mechanics, electrochemistry and other fields [4–6]. However, the deposition of adherent high-quality diamond film onto substrates represents a considerable challenge because of poor adhesion and low nucleation density. Sein et al. [7] employed a chromium interlayer to improve the adhesion. Ali et al. [8] used a pulsed laser irradiation method to provide additional energy to the incoming species to increase the adhesion. Diamond films with good adhesion effectively improve the anti-wear and anti-erosion abilities of Ti and its alloys [9,10]. High-quality diamond film has become an attractive material for electrodes in electro-oxidation and electro-analysis, because of the high over-potential of H_2 and O_2 evolutions and low background noise. Additionally, the nucleation of diamond is an important step in the growth of diamond films because it strongly affects their quality and morphology [11–14].

Hot filament chemical vapor deposition (HFCVD) is the simplest low-pressure CVD method; it can be used easily to grow large-area diamond films, and the required equipment is simple and can be operated at low cost [15]. The interface properties, morphology, and crystalline quality of CVD diamond films depend strongly on the growth conditions, including gas composition, substrate temperature, working pressure, and gas flow rate. Therefore, much effort has been made to produce microcrystalline and nanocrystalline diamonds by manipulating the deposition process, including the nucleation and growth in mixtures of hydrocarbon (such as,

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CH_4) and hydrogen with or without dilution by noble gases such as Ar [16–18], oxygen [19] or N_2/CH_4 as reactant gas [20].

The growth of diamond films by CVD in H_2/O_2/CnHm systems is an active area of research. Hydrogen atoms have a critical role in the deposition process and in determining of the properties of CVD diamond films. Several works have focused on the incorporation of hydrogen in polycrystalline diamond films [21–23]. Recently, Yang et al. [24–26] successfully deposited high-quality films on an Si substrate at temperatures of 250 °C with a high growth rate using graphite etched by hydrogen as a carbon source in an HFCVD reactor without plasma discharge [24,25], and in a microwave plasma reactor [25,26]. They further suggested that activated hydrocarbon radicals formed through in situ etching of graphite by atomic hydrogen promote diamond growth [27]. The field electron emission characteristics of the diamond films exhibit improve as the hydrogen flow rate declines. Adding oxygen is well known to be able to increase the diamond content of microcrystalline diamond (MCD) films deposited by CVD in $O_2/(CH_4 + H_2)$ systems, improving their mechanical quality [28,29]. The effect of oxygen on the emission of electrons from nanocrystalline diamond (NCD) films has also been described [30,31]. As revealed recently by Shen et al. [32], oxygen has a significant positive effect on the elastic properties of non-diamond films, and the growth rate declines sharply as the amount of oxygen increases above around 4%. However, to the best of author's knowledge, no study is available on how adding H_2 and O_2 influences the morphology, crystalline quality, corrosion and wear-corrosion resistance properties of CVD diamond films. Accordingly, the aim of this work is to evaluate the corrosion and wear-corrosion resistance of CVD diamond films with and without the addition of H_2 or O_2 in 1 M H_2SO_4 + 1 M NaCl solution by electrochemical polarization. The relationship between the surface structure of the CVD diamond films and their corrosion and wear-corrosion resistance property is also discussed.

2. Experimental

2.1. Deposition and characterization of diamond films

The diamond films studied herein work were deposited on the (1 0 0) plane of single crystalline silicon substrates by hot filament chemical vapor deposition. The substrates were polished with diamond micro-powders to promote nucleation. Runs in which diamond was grown from methane (methane flow rate, 10 sccm) were 8 h long then 10 min of hydrogen or oxygen flow at a flow rate of 100 sccm was applied to compare the quality of the diamond films. The optimal deposition conditions were, substrate temperature of 890 °C deposition pressure of 5 kPa and filament temperature of 2000 °C. The thickness of the resulting diamond films, measured by gravimetric analysis, and was 10.0 ± 0.3 μm. The diamond films were characterized using a variety of methods. Raman spectroscopy and X-ray diffraction (XRD) were employed to elucidate the bonding environments, the including crystalline quality and purity, and the phase and crystallinity of the samples. Raman spectra were obtained using a Jobin Yvon LabRAM-HR Raman spectrometer with an argon laser wavelength of 514.5 nm in the wavelength range 800–2000 cm^{-1}. The laser spot size was about 2 μm in diameter. XRD measurements were made using a Siemen D5000 X-ray diffractometer with Cu Kα radiation (0.15418 nm). A Quesant Q-250CL atomic force microscope (AFM) was used to characterize the surface morphology of the deposited diamond films. The mechanical properties of the samples were measured using a Criso-UMIS nano-indentation test system, and the applied load was 480 mN. The nanohardness of the specimen was evaluated by averaging over four experimental runs.

2.2. Electrochemical corrosion and wear-corrosion tests

Electrochemical corrosion properties were studied using potentiodynamic polarization. The sample size was 1 cm × 1 cm. The potentiodynamic polarization curves were obtained by scanning from 250 mV_{SCE} below OCP to 1600 mV_{SCE}, at a scanning rate of 1 mV s^{-1}. All potentials referred to the saturated calomel electrode (SCE), with platinum wire as the counter electrode. A potentiostat (EG & G Model 273A) with analytic software were used. The wear-corrosion behavior of the specimens was elucidated by performing the same potentiodynamic polarization scan during wear. All of the specimens before and after the tests were cleaned and weighed following the ASTM G1-90 standard method [33]. A block-on-ring wear-corrosion testing apparatus [34,35] was employed to measure the friction coefficient, μ, and the electrochemical characteristics. The friction force (F) was measured using a load cell and, using a personal computer, was recorded and automatically divided by the applied load (N) to yield the friction coefficient ($\mu = F/N$). Specimens were placed in contact with a rotating ring, which was made of sintered Al_2O_3 ceramic with an external diameter of 22.5 mm, an internal diameter of 13.0 mm and a width of 13.5 mm. The applied load (100 g_f) and sliding speed (0.12 m s^{-1}, or 100 rev min^{-1}) were fixed in the wear-corrosion tests. The sliding distance was fixed at 216 m. The wear-corrosion test cell contained 4 L of aerated 1 M H_2SO_4 + 1 M NaCl solutions. The chemicals used herein were all of analytical reagent grade. Also, deionized water (≥18 MΩ) was used to prepare the testing solution.

3. Results and discussion

3.1. Characterization of diamond films

Raman spectroscopy is a convenient method for analyzing the phase carbon materials, as each phase yields specific spectral peaks. Fig. 1 presents the Raman spectra of the diamond films grown with the addition of different gases—hydrogen and oxygen addition, denoted CVD, CVD + H_2 and CVD + O_2, respectively. A sharp peak at around 1333 cm^{-1}, characteristic of the sp^3-bonded diamond phase, is clearly observed in all of the spectra, revealing that the diamond coatings were of high quality. The full width at half maximum