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Influence of temperature on structure as well as adhesion and friction and wear behavior of hydrogenated carbon nitride films prepared on silicon substrate

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ABSTRACT

Hydrogenated-carbon nitride (CN_x:H) films were synthesized on silicon substrate in a large quantity by the pyrolysis of ethylenediamine in a temperature range of 700–950 °C. The influence of temperature on the morphology, structure, adhesion to substrate, and friction and wear behavior of CN_x:H films was investigated. It has been found that CN_x:H films obtained at 700 °C and 800 °C are amorphous, and those prepared at 900 °C and 950 °C consist of carbon nitride nanocrystal. Besides, CN_x:H film sample obtained at 700 °C has the maximum N content of 9.1 at.% but the poorest adhesion to Si substrate, while the one prepared at 900 °C has the lower N content and the highest adhesion to substrate. As a result, nanocrystalline CN_x:H (nc-CN_x:H) film synthesized at 900 °C possesses the best wear resistance when slides against stainless steel counterpart. N atom is incorporated into the graphitic network in three different bonding forms, and their relative content is closely related to temperature, corresponding to different adhesion as well as friction and wear behavior of the films obtained at different temperatures. Furthermore, the friction coefficient and antiwear life of as-deposited CN_x:H films vary with varying deposition temperature and thickness, and the film with thickness of 1.3 μm, obtained at 900 °C, has the longest antiwear life of over 180,000 s.

1. Introduction

Many efforts have been made to synthesize carbon nitride nanocrystals with special characteristics and potential applications in various high-tech fields; and it has been recognized that the structural, electrical, optical, and mechanical properties of carbon films can be effectively modified by incorporating hydrogen to manipulate the bonding configuration [1,2]. This is because hydrogen affects the ratio of sp^2- and sp^3-hybridized carbon atoms in carbon films and may also create N—H bonding and influence the degree of surface contamination by oxygen [3]. Resultant CN_x:H films are of particular significance in the field of nanotribology, due to their possible application as ultrathin protective overlayers for magnetic film rigid disks [4]. Unfortunately, contradictory results have been published regarding an increase [5,6], no change [7] or a decrease [8,9] of the friction coefficient with the incorporation of nitrogen in CN_x:H films, although it has been widely recognized that incorporating nitrogen atom in CN_x:H films results in improved wear resistance [5–9]. Chemical vapor deposition (CVD) is the most extensively used method to fabricate N-substituted carbon structures, which relies on catalytic pyrolysis of C (graphite) or CN gas-phase precursors (methane, nitrogen gas and ammonia) under N-rich atmosphere and is usually carried out under relatively lower temperatures (<200 °C); and resultant CN_x:H films are generally amorphous and has poor adhesion to substrate [10,11]. Maya et al. obtained a carbon nitride with trigonal-coordinated carbon *via* the pyrolysis of high N-containing organic compounds such as melamine, dicyandiamide and tetracynanoethlene at 700 °C and 225 MPa [12]. Nesting and Badding prepared amorphous carbon nitride with 38 at.% nitrogen by laser heating tetracynanoethylene (TCNE; molecular formula C_6N_4), a molecular precursor, under a pressure of up to 40 GPa [13]. The above-mentioned researches demonstrate that, while carbon nitrides with significant amount of nitrogen can be achieved under relatively high pressure, the deposition temperature is a critical factor for synthesizing carbon nitride nanocrystals; and in particular, deposition temperature has a significant effect on the N content, structure, and crystallinity of carbon nitride [14]. However, the mechanisms responsible for this phenomenon are still unknown. Moreover, although it has been found that the ratio of nitrogen to carbon may play a key role in determining the friction and wear behavior of CN_x films [5], further work is urgently needed to reveal the dependence of the friction and wear behavior of CN_x films on reaction temperature and to correlate their microstructure with wear resistance. Several studies [15,16] have shown that the mechanical properties of CN_x:H films depend

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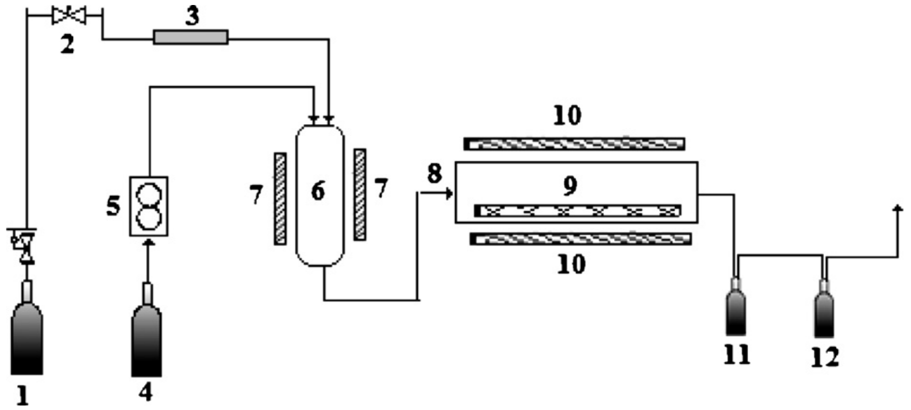

Fig. 1. Scheme of the set-up for preparing CN$_x$:H films. 1-Argon cylinder; 2-Needle valve; 3-Flowmeter; 4-Ethylenediamine <app:ds:ethylenediamine> liquid; 5-Peristaltic pump; 6-Premixing tube; 7-Heater band; 8-Quartz tube; 9-Substrate; 10-Tube furnace; 11-Buffer bottle; 12-Liquid absorbing bottle.

heavily on the nitrogen:carbon ratio, and increasing nitrogen content produces softer material [17]. Moreover, Chan et al. [18] have observed that increasing nitrogen content leads to increase of both density and size of graphitic domains. Those studies indicate that the nitrogen content may play an important role in affecting the friction coefficient and wear rate of carbon nitride films. In our experiments, however, we have found that the content of nitrogen seems to have only minor effect on the wear resistance of as-prepared CN$_x$:H films, and the friction coefficient of CN$_x$:H films on silicon substrate is heavily dependent on the microstructure in relation to deposition temperature.

With those perspectives in mind, we selected ethylenediamine as a liquid-phase nitrogen precursor to prepare uniform CN$_x$:H films *via* chemical vapor deposition at 700–950 °C. The dependence of the morphology, structure, bonding configuration and friction and wear behavior of as-prepared film samples on temperature was investigated in detail. It has been found that the excellent friction-reducing ability and wear resistance of CN$_x$:H films are mainly due to the formation of nanocrystalline carbon nitride in association with the introduction of nitrogen atoms to sp^2-bonded carbon. This finding, hopefully, is to add to knowledge about CN$_x$:H films and provide reference to their tribological application as well.

2. Experiment

2.1. Preparation of CN$_x$:H films

A two-stage process was established to prepare CN$_x$:H films in a large quantity. Firstly, CN$_x$:H films were deposited on silicon substrate using a CVD apparatus shown in Fig. 1. After Ar flow was inlet to remove the air in the reactor, ethylenediamine (Tianjin Kermel Chemical Reagent Company Ltd., Tianjin, China) vapor flow was introduced into the premixing tube with a peristaltic pump at a rate of 0.50 mL/min. The vapor mixture of Ar and ethylenediamine was introduced into the CVD chamber after the temperature rose above the boiling point of ethylenediamine, followed by the deposition of CN$_x$:H films for about 30 min at a pre-set temperature. Resultant CN$_x$:H films were then calcinated *in situ* at the same pre-set temperature for about 30 min while Ar flow was continuously introduced into the chamber but ethylenediamine flow was closed. As-obtained CN$_x$:H films are denoted as CN-700, CN-800, CN-900, and CN-950, respectively, where numerical suffixes refer to deposition and calcination temperature of 700 °C, 800 °C, 900 °C, and 950 °C. The thickness of the CN$_x$:H films can be manipulated by properly adjusting the dosage of ethylenediamine in the mixed gas; and a higher content of ethylenediamine usually corresponds to a larger thickness of the films.

2.2. Characterization of CN$_x$:H films

An SPA400 atomic force microscope (AFM) was employed to observe the morphologies of CN$_x$:H films deposited on silicon wafer and to evaluate their surface roughness as well. AFM analysis was carried out in tapping mode with commercial silicon microcantilever probe under ambient conditions (24 ± 2 °C). The tip radius and spring constant of the probe are less than 20 nm and 2.0 N/m, respectively.

The crystalline structure and size of as-prepared CN$_x$:H films were analyzed by means of powder X-ray diffraction (XRD; X'Pert Pro X-ray diffractometer, Cu Kα radiation, $\lambda = 0.154$ nm, applied current 40 mA, voltage 40 kV) in a scan range (2 theta degree) of 10–80° at a scan rate of 2.4°/min. All peak data measured by XRD analysis were assigned to known crystalline phases by comparing with those of JCPDS database.

X-ray photoelectron spectroscopy (XPS) was used to identify the chemical states of the elements on the surface of the CN$_x$ films. An AXIS ULTRA multi-technique electron spectrometer (Kratos, UK; Al Kα X-ray source, $h\nu = 1486.6$ eV; pass energy 40 eV) was used. The binding energy of C1s (284.8 eV) was used as reference. No sputtering etching was performed before the measurement. The relative atom percentage composition of CN$_x$:H film surfaces is provided by the results of quantitative XPS analysis. The quantitative analysis of the surface elemental composition was accomplished by taking into account the XPS sensitivity factors with a computer program attached to the facility (Vision 2).

Raman spectra were collected with a confocal micro-Raman spectrometer (Renishaw R-1000) equipped with a charge-coupled device (CCD) detector. A 457.5 nm solid-state laser was focused onto the surface of the samples through a 50 times objective microscope lens. The scattering light was collected in a backscattering geometry at a spectral resolution of 1 cm^{-1}. The Raman spectra were curve-fitted based on three Gaussian curves to identify peak positions and intensity.

A Fourier transform infrared spectrometer (FTIR) (AVATAR360) was used to analyze the components of the typical resultant CN$_x$:H films. Structural characterization of CN$_x$:H films was conducted by means of scanning electron microscopy (SEM, JEOL JSM-5600LV; acceleration voltage 20 kV), where the samples for cross-sectional SEM observation were prepared by mechanical cleaving. The thickness of the CN$_x$:H films was estimated from relevant cross-sectional SEM images. The amount of hydrogen of the films was determined with a PE2400II elemental analyzer, where a known amount of the film sample was burnt and then the fractions of water vapor, carbon dioxide and nitrogen in the combustion gas were determined by chromatographic analysis.