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Onion-like carbon films endow macro-scale superlubricity

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ABSTRACT

Onion-like carbon films were prepared by constant current high-frequency dual-pulsed plasma enhanced chemical vapor deposition technique. Owing to the unique carbon onions both in bulk and debris of nanostructured carbon matrix, the films not only showed a super-high elastic recovery up to 92%, but also obtained a super-low friction coefficient below 0.01 and wear rate about $6.41 \times 10^{-18}\,\mathrm{m^3/Nm}$ in ambient atmosphere. The carbon onions achieved an incommensurate contact and played as "molecular bearing" in the friction process, resulting in both super-low friction and wear rate.

1. Introduction

Achieving low friction and wear between moving surfaces are of great physical and technological interests, since they are directly responsible for the efficiency, life, and accuracy of the mechanical system [1–4]. Superlubricity—the vanishing of sliding friction—firstly proposed by Hirano in 1990s, is a significant mean to essentially deal with the friction and wear [5]. Until now, superlubricity phenomenon has been observed in 1D (carbon nanotubes, graphene nanoscrolls) and 2D (highly oriented pyrolytic graphite (HOPG), MoS_2 monolayers, graphene, etc.) materials [6–9]. In these materials, friction on carefully-prepared C-plane is approximately to zero under incommensurate contact, which is also known as "structure superlubricity" [6]. However, for most industrial applications, additional properties, such as larger scale, bearing capacity, environmental and humidity stability are required [8, 9]. Diamond like carbon (DLC) is the most promising engineering superlubricity materials because it can considerably reduce friction coefficient ($\mu \leq 0.01$ under dry and vacuum environment), extend the lifetime of moving parts and meet the requirement of industrialization [10]. Recently, extensive efforts are devoted to designing special nanostructure in DLC to achieve macro-scale superlubricity. Nanostructure DLC films benefitted from special nanostructures, such as fullerene-like carbon [11], graphene sheets [12,13] and dual nanostructures [14], show an obvious progress of low friction and wear. Among carbon-based structures, fullerene family is considered to be used as advanced nano-lubricants insignificantly, due to the unique spherical structure and high chemical stability [15]. It is predicted that carbon onions (COs) may have some particular tribological properties that are superior to traditional solid lubricants, especially under crucial conditions, such as high pressure [16], high vacuum [17] or macroscale sliding contact conditions [18]. The molecular dynamics simulations showed that rolling friction enabled by the spherical molecules reduced friction coefficient by 10^2–10^3 orders of magnitude than sliding friction [19]. The study by Ofer Tevet using a current in situ high resolution scanning electron microscopy indicated that rolling was not only plausible but also an important friction mechanism for giant fullerene [20]. Recently, Sumant found macroscale superlubricity could be enabled by graphene and nanodiamond, due to the formation of graphene nanoscrolls [8]. However, the only graphene cannot form such coiled structure, and the friction coefficients could be much high ($\mu > 0.2$) [8]. Therefore, the coiled structure is the key structural factor to superlubricity.

According to our current understanding, introducing the superlubricity elements in thin films may greatly reduce the friction coefficient and wear rate. Hitherto, many methods are developed to construct carbon fullerene nanostructured thin films: (1) direct-adding fullerenes into the films, such as liquid deposition [21]. (2) self-assembly [22]. (3) plasma vacuum deposition, using fullerene as a precursor to prepare dense films [23, 24]. (4) high-pressure of fullerene [25]. Nevertheless, these processes can hardly get smooth, excellent overall performance thin films and even may also result in structural damage. Therefore, preparation of dense and well-formed carbon onion films is a great challenge. Previous studies showed that fullerene-like carbon can be formed by plasma-enhanced chemical vapor deposition (PECVD) [11]. The grain size or order degree of deposited materials increases with the plasma excitation frequency [26–28]. Thus high-frequency power supply system can increase the crystallinity of fullerene like structures to create onion like nanostructures. This work firstly fabricates

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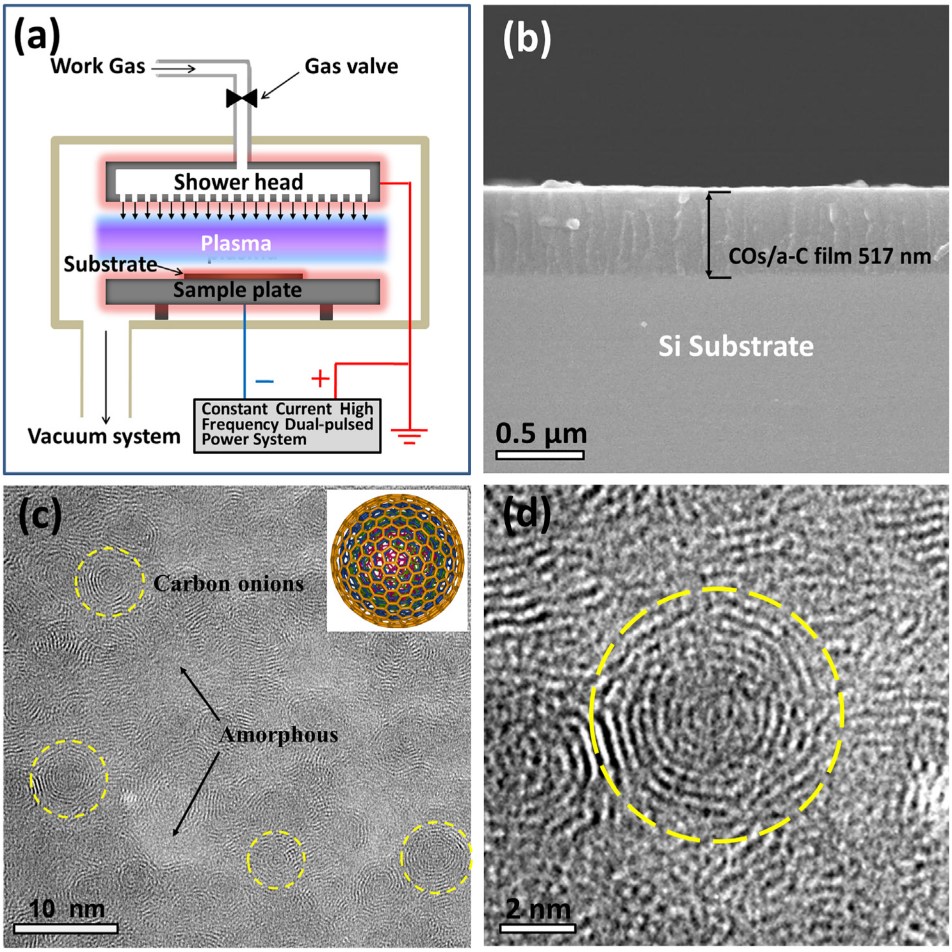

Fig. 1. (a) Model of the plasma-enhanced chemical vapor deposition (PECVD) technique. (b) FESEM image of cross section of COs/a-C films. (c) HRTEM images of COs/a-C films, insert is the model of carbon onions. (d) HRTEM images of a single carbon onion in the COs/a-C films.

composite nanostructure carbon films with well-formed carbon onions (COs/a-C) by PECVD technique equipped with a constant current high-frequency dual pulse power system. It has been found that macro-scale superlubricity can be enabled by COs/a-C films under humid air, which could match the requirements of actual working conditions. The friction mechanism of the COs/a-C films is discussed, especially the role of COs.

2. Experimental methods

2.1. Film preparation

The COs/a-C films with a thickness of about 500 nm were fabricated on Si (100) substrates in a pure methane (CH_4, 99.99%) discharge. The deposition chamber was pumped down to 10^{-4} Pa, followed by introducing working gas at 20 sccm with a pressure of 10 Pa. The distance between the upper plate and the sample tray was 5 cm. The power supply (JX-MSB-H, JINXIN, CHINA) operated in a constant current mode under negative voltage of 500 V with a current of 0.8 A (average output power of 400 W). The frequency is up to 200 kHz, and the duty cycle is 0.6.

2.2. HRTEM sample preparation

The high-resolution transmission electron microscope (HRTEM) sample, with a thickness of 20 nm, prepared on freshly cleaved NaCl wafers. In order to avoid metal contaminate, the substrate holder and chamber wall were firstly coated by carbon films with a thickness about 1000 nm before samples deposition.

2.3. Structure characterizations

The structural were analyzed on a high-resolution transmission electron microscope (HRTEM, Tecnai-G2 F30, FEI, US), equipped with energy-dispersive X-ray analysis (EDX, Oxford Instrument, UK). The detailed bond structure was collected by micro-Raman with a LABRAM HR 800 micro-spectrometer at an excitation wavelength of 532 nm (2.3 eV). The power density of the sample was controlled carefully at 0.5 MW m^{-2} to avoid sample surface heating.

2.4. Nano-indentation tests

The mechanical properties of the as-deposited films were measured by nanoindentation (Hysitron Ti-950) with a trigonal Berkowich diamond tip. The maximum indentation depth was controlled about 50 nm (1/10 of the film thickness). The elastic recovery R is defined as Formula (1), where d_{max} and d_{res} are the maximum displacements at maximum load and the residual displacements after unloading, respectively.

$$R = (d_{max} - d_{res})/d_{max} \times 100\% \quad (1)$$

2.5. Tribological characterization

The tribological performance of the specimen was evaluated by the ball-on-disk method (against Al_2O_3 ball with a load of 10 N, at a humidity of 30%, with a frequency of 10 Hz). The wear rate (I) of the films was measured by a three-dimensional profilometer (NanoMap-D, APE