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Synthesis of carbon films with ultra-low friction in dry and humid air

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Abstract

Using pulsed dc magnetron sputtering, we synthesized hydrogenated amorphous carbon films with and without sulfur doping. These films were smooth and amorphous, with low compressive stress (<1 GPa). Auger electron spectroscopy confirmed the incorporation of sulfur, and X-ray photoelectron spectroscopy showed that sulfur atoms are chemically bound. Most significant, ball-on-flat tribo-testing showed that hydrogenated carbon films doped with 5 at.% sulfur have ultra-low friction coefficients (<0.01) in air with relative humidity from 0% to 50%.

Keywords: Hydrogenated carbon films; Sulfur doping; Friction; Magnetron sputtering

1. Introduction

Hydrogenated amorphous carbon films (CH_x) have been extensively investigated due to their wide range of properties. These films can be synthesized through a variety of physical and chemical techniques. Tribological properties of these films depend on testing conditions (environment, load, speed and geometry), film structure and composition, and surface roughness [1,2]. Heavily hydrogenated carbon films deposited by chemical vapor deposition have been shown to provide ultra-low friction coefficients (<0.01) in vacuum and dry nitrogen environments. This ultra-low friction between two coated surfaces has been attributed to hydrogen-terminated surfaces with weak van der Waals interaction, resulting in weak adhesion and hence low shear strength against sliding [3–7]. Their friction coefficients increase rapidly in the presence of oxygen and humidity. Oxygen can interact with both the carbon and hydrogen atoms [8,9]. Tribochemical reactions resulting in oxidation of the film have also been observed to increase friction. Atomic oxygen increases the friction coefficient much more than molecular oxygen [10,11]. Tribochemical oxidation from oxygen or water has also been observed to affect the transfer layer, even at low partial pressures, increasing friction coefficients. This is attributed to the oxygen removal of sp^2 carbon atoms from the transfer layer [12,13]. The strong dependence on humidity has been attributed to viscous and capillary forces induced by adsorbed water [14].

There have been efforts to mitigate the humidity problem. Silicon, fluorine, boron, gold, and titanium doping have been attempted, but they have only marginal effects on the moisture sensitivity of CH_x films. Friction coefficients of 0.04–0.1 were measured in ambient air, at least 10 times higher than those measured in dry air by Erdemir et al. [1,15–18]. Silicon and boron dopants are thought to form a silicon oxide or boric acid lubricous layer on the surface in humid air, decreasing the ambient friction coefficient [1,19,20]. Gold acts as a solid lubricant because of its low shear strength [21]. Reduction in the surface energy using fluorine-doped films is believed to be the primary reason for the reduced sensitivity of friction towards moisture [22].

Tagawa et al. observed a direct link between water coverage on a hydrogenated carbon surface and friction coefficient. The friction coefficient increased markedly when the surface water coverage exceeded about one monolayer [23]. Shulka et al. measured the adsorption of water to be ~1.5 monolayers on hydrogenated carbon films at 60% relative humidity [24]. Therefore, reduction in the surface water coverage under humid conditions may allow these films to retain their low friction properties. The ability of certain surface dopants to suppress gas adsorption is well-documented in the surface science literature, due to physical site-blocking or modification of surface electronic properties [25]. In principle, one can minimize water

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adsorption by proper surface texturing [26,27], but this may lead to high friction due to mechanical interlocking or plastic deformation of asperities.

Here, we report the synthesis and characterization of sulfur-doped hydrogenated carbon films. These films exhibit ultra-low friction behavior in ambient humid air. We believe that this is due to suppressed water adsorption on these sulfur-doped hydrogenated carbon film surfaces.

2. Experimental

Hydrogenated carbon films were deposited in a single-cathode unbalanced magnetron sputter-deposition system with a base pressure of better than 6.6×10^{-6} Pa (5×10^{-8} Torr). A 5-cm-diameter pure graphite target was used. The target power was set at 100 W pulsed at 150 kHz (80% duty cycle), with the positive voltage set at 10% of the negative voltage. The sputter-gas was an argon–hydrogen–hydrogen sulfide mixture. The argon–hydrogen ratio remained constant at 15% hydrogen, balance argon at a sputtering pressure of 6 mTorr (0.8 Pa). For results reported in this paper, the hydrogen sulfide partial pressure was set at 0.02 mTorr, resulting in 5.0 at.% sulfur concentration in these carbon films. Low-resistivity silicon (100) wafers and 6.35-mm stainless steel ball bearings were used as substrates. Prior to carbon film deposition, the ball bearings were coated with 75 nm of silicon by sputtering to improve film adhesion. All substrates were ultrasonically cleaned in acetone and methanol before being introduced into the deposition chamber and sputter-cleaned in argon before deposition. The substrate was pulse-biased at −25 V, 20 kHz to improve the efficiency of ion bombardment during film growth. The film thickness was set at 1.0 μm for all depositions.

Auger spectra were taken using a double-pass cylindrical mirror analyzer (Staib Instruments). X-ray photoelectron spectroscopy was performed on an ESCA Probe (Omicron). Friction properties were measured using a CETR Micro-Tribometer (UMT) in a standard ball-on-flat configuration at room temperature. The sliding speed was 0.01 m/s. Both the ball and flat were coated. The tribometer was enclosed in a glove box to enable controlled atmosphere testing. Humidity was reduced by the introduction of dry air. Surface roughness was measured with a Nanoscope IIIa atomic force microscope (Digital Instruments) in contact mode. Hardness and elastic modulus were measured using a nanoindentor (Hysitron) with the supplied software, which analyzed the load–displacement curves with the method of Pharr and Oliver [28].

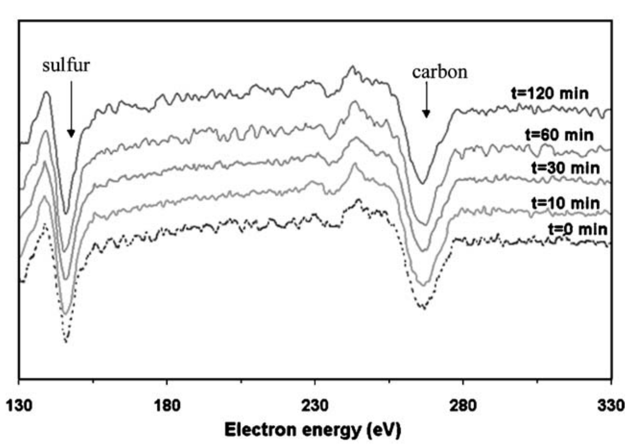

Fig. 1. Auger analysis of 5 at.% sulfur-doped hydrogenated carbon films. The bottom spectrum was taken after sputter-cleaning at room temperature, followed by a series of Auger spectra taken after the indicated time of annealing at 300 °C. There is no change in the sulfur-to-carbon ratio as a result of annealing.

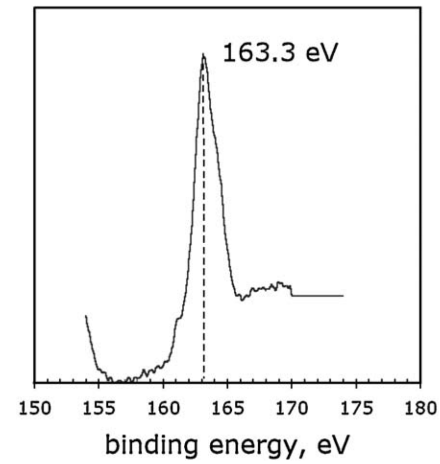

Fig. 2. Sulfur 2p core level spectrum from a sulfur-doped hydrogenated carbon film.

3. Results and discussion

Sulfur incorporation was verified using Auger electron spectroscopy. As illustrated in Fig. 1, the surface composition is stable with respect to annealing at 300 °C. Auger sputter-profiling showed that sulfur is uniformly distributed within these films. Separate Rutherford backscattering measurements showed that these films contained ~30 at.% hydrogen. X-ray

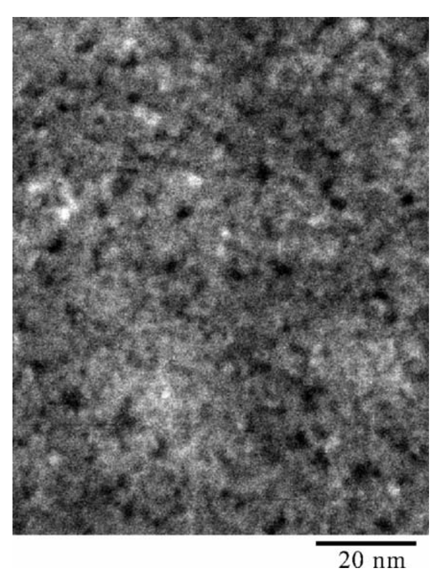

Fig. 3. Transmission electron micrograph from a sulfur-doped hydrogenated carbon film.