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Nano-scratch resistance study of nitrogenated amorphous carbon films prepared by unbalanced magnetron sputtering

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Abstract

Nitrogenated amorphous carbon (a-CN_x) films prepared by unbalanced magnetron sputtering (UBMS) have been investigated and compared with those prepared by conventional magnetron sputtering (CMS). The nitrogen-to-carbon ratio in deposited films increases from 0 to 0.22 as the N_2/Ar gas flow ratio varies from 0 to 8/17. Raman spectroscopy and atomic force microscopy nano-scratch resistance test were used to characterize the a-CN_x films. As N content in the film increases, the G peak width decreases from 183 to 170 cm^{-1}, the I_D/I_G intensity ratio increases from 2.2 to 2.9. The a-CN_x films prepared by UBMS show a much lower scratching depth than those prepared by CMS. The pure carbon prepared by UBMS shows the lowest scratching depth, which can be interpreted by the high sp^3 fraction of carbon atoms in the film.

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1. Introduction

Carbon coatings are currently used as a smooth and protective coating on the magnetic disk and head against wear and corrosion as well as against local charging. The rapidly increasing storage density of magnetic thin film media will soon require carbon overcoats of only 2 nm or less in thickness. The carbon overcoats are either pure carbon or carbon based composite with hydrogen or nitrogen incorporation. The carbon films normally have an amorphous structure with a wide range of sp^3 fraction of carbon atoms. The overcoats for magnetic media are presently made by magnetron sputtering, chemical vapor deposition and ion beam deposition. Filtered cathodic vacuum arc technique is another choice for the overcoat for magnetic head.

Conventional magnetron sputtering (CMS) is still one of deposition techniques used for carbon coatings because of the high deposition rate and homogeneity of the films. Several attempts have been reported to improve the hardness and wear resistance of carbon overcoats. Incorporation of nitrogen in amorphous carbon films has shown positive influence on the scratching resistance of carbon film [1]. Amorphous carbon film prepared by unbalanced magnetron sputtering (UBMS) has been reported to have a hardness of 22 GPa [2]. In the setting of UBMS, some electrons in the plasma are no longer confined to the target region, but are able to follow the magnetic field lines and flow out towards the substrate. As a result, ion bombardment at the substrate increases with a consequent improvement in coating structure. The use of unbalanced magnetron configurations allows high ion currents to be transported to the substrate so that coatings of excellent quality can be deposited [3]. In this work, nitrogenated amorphous carbon (a-CN_x) films were synthesized by UBMS technique. The structural and mechanical properties of a-CN_x films were investigated as a function of N_2/Ar gas flow ratio used during the film deposition.

2. Experimental details

a-CN_x films were prepared using a chamber with UBMS in a commercial single disk sputtering system (BPS,

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Circulus M12). After the sputtering chamber was evacuated to a base pressure less than 5.0×10^{-5} Pa, 99.999% pure N_2 and Ar gases were introduced to the chamber in different gas flow rate ratios while keeping a constant total gas flow rate of 25 sccm. As the N_2/Ar gas flow ratio changed from $\frac{0}{25}$ to $\frac{8}{17}$, the working gas pressure varied from 0.50 to 0.43 Pa, which is due to higher pumping speed for nitrogen gas. The films were prepared under negative bias conditions at room temperature in a DC power mode with an input power of 750 W. The negative bias was kept at 150 V for the samples prepared at different N_2/Ar gas flow ratios and varied from 0 to 200 V for the different bias samples. The films with thickness about 20 nm were prepared at room temperature on clean disk shaped AlMg metal substrate.

The thickness of the a-CN_x films was measured with a surface profilometer and then was controlled by adjusting deposition time. The N content in the deposited films was determined by X-ray photoelectron spectroscopy (XPS) using a monochromatic Al Kα (1486.6 eV) X-ray radiation (PHI Quantum). The Raman spectra were excited using the 514.5 nm line of an Ar^+ laser and collected in a back scattering geometry on a charge coupled detector (CCD) using a Renishaw micro-Raman System 1000 spectrometer. A laser output of 20 mW was used, which resulted in an incident power at the sample of approximately 1.5 mW over an area of several micrometers. Spectral resolution of the spectrometer (half-width at half-maximum) is 2.0 cm^{-1}. The scratching resistance of the films was measured by atomic force microscopy (AFM) nano-scratch. A diamond-tipped cantilever was used to create and to image the scratches. All the films were scratched by the diamond tip with a same trig threshold voltage of 0.3 V. The scratching line is 1 μm long. The film surface morphology before and after scratching was observed using tapping mode AFM measurement with the same diamond-tipped cantilever. The root mean square (RMS) roughness was obtained for the as-deposited films using the digital image-processing package attached to the system over an image area of $4 \times 4\,\mu m^2$.

3. Results and discussion

Fig. 1 shows the effect of N_2/Ar gas ratio on the deposition rate and on the nitrogen-to-carbon ratio in the deposited a-CN_x films. The N_2 content in the sputtering gas has an influence on the growth rate of the films. The deposition rate (Fig. 1(a)) increases from 0.64 nm/kW s, in a pure Ar discharge, to the maximum value of 1.11 nm/kW s in a discharge with an N_2/Ar gas flow ratio of $\frac{8}{17}$. This variation of the deposition rate versus the N_2/Ar gas flow ratio has already been observed in reactive magnetron sputtering [4–6]. The increase in the deposition rate may be due to the promoted formation of C–N radicals at target surface (i.e. chemical sputtering process) and to an increase of the physical sputtering yield of the graphite target. During the film deposition, a DC power mode was used

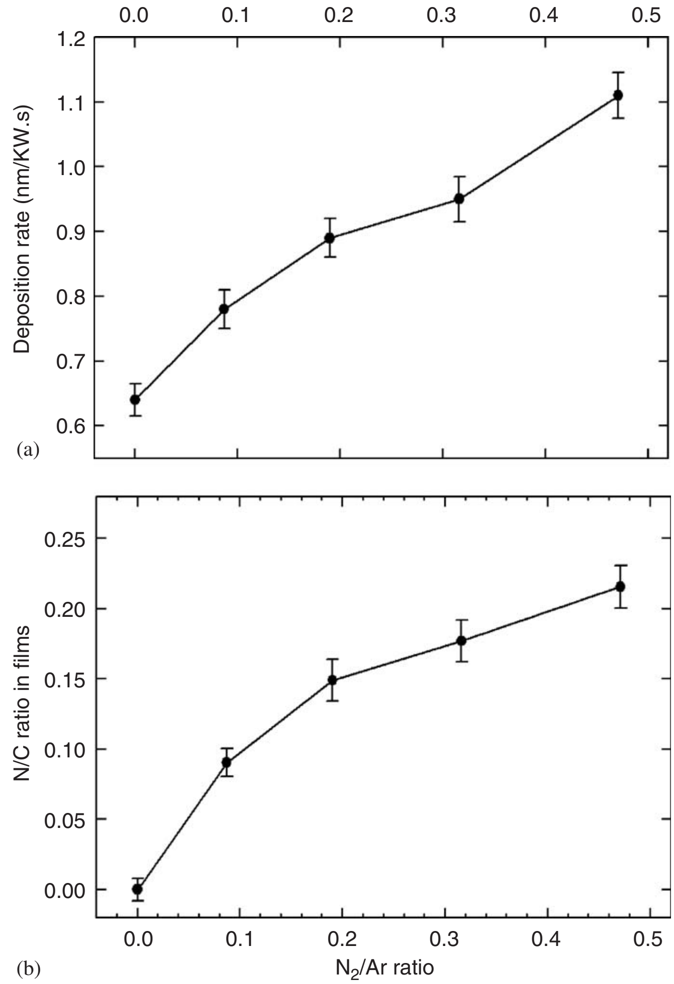

Fig. 1. Dependence of (a) deposition rate and (b) nitrogen-to-carbon ratio in the film on the N_2/Ar gas flow ratio.

with a constant input power of 750 W. Meanwhile the electrical current or the electrical voltage between the anode and the cathode varies with the change of N_2/Ar gas flow ratio. The electrical voltage increases from 620 V in a pure Ar discharge to 700 V at an N_2/Ar gas flow ratio of $\frac{8}{17}$. The higher electrical voltage is due to the lower working gas pressure (0.43 Pa) and to the higher energy needed to ionize the N_2 gas.

The XPS analysis revealed the presence of C, N and O atoms in the films. The presence of oxygen (approximately 5 at %) is mainly a surface pollution due to the exposure of the films to air prior to analysis [4]. The presence of N atoms (approximately 1.6 at %) was detected in the surface of the carbon film prepared with pure Ar gas. Besides surface pollution, the existence of dangling bonds on the fresh carbon surface may result in O and N absorption in the surface. For a-CN_x films, the nitrogen detected by XPS measurement contains two parts: absorbed in the surface and existing in the films. It is assumed that the absorbed nitrogen in the surface is approximately the same as that of the pure carbon film. The N content in the a-CN_x films was determined by subtracting absorbed nitrogen in the surface