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Surface smoothing of sputter deposited amorphous CN_x films by silicon addition

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Abstract

Amorphous carbon nitride (CN_x) films with silicon addition up to 16 at.% are sputter deposited on Si(100) substrate, and the surface morphology is studied with scaling method based on atomic force microscopy. The surface roughness σ, the roughness exponent α, and the lateral correlation length ξ decrease with silicon content of the films, reaching 0.33 nm, 0.80 and 50 nm, respectively, for the film with [Si] = 16 at.%. The addition of silicon in the films leads to additional Si–N, Si–C–N and C≡N bonds revealed by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. The films undergo a structural transition from columnar to smooth morphology in cross-section with silicon addition demonstrated by field emission scanning electron microscopy. Nano-sized clusters sparsely dispersed in amorphous matrix of the film with [Si] = 16 at.% are observed by high-resolution transmission microscopy. According to the surface growth mechanism in which surface diffusion and geometrical shadowing drive structural and morphological evolution of the sputter deposited films, surface smoothing of the amorphous CN_x films by silicon addition is explained by the formation of Si–N and Si–C–N bonds that impede surface diffusion of the adsorbed species during film growth, which leads to the reduced size of the columnar structures.

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1. Introduction

Carbon nitride (CN_x) thin films have been researched since last decade due to their interesting mechanical, electrical and optical properties [1–3]. The films obtained through a wide range of deposition techniques and conditions are mostly amorphous in structure. One class of the potential applications for amorphous CN_x films is the wear protective coatings, e.g. the protective overcoat layer for magnetic thin-film rigid disks [4,5]. In such cases, apart from the excellent mechanical properties, the smooth surface is also crucial for the better tribological performance of the protective CN_x films in service. However, the surface roughness of CN_x films generally increases with the nitrogen concentration, because the incorporation of nitrogen in the films can increase the size and number of the clusters of graphitic domains that lead to substantial roughening at the film surface [6].

In the studies of superhard nanocomposite MeSiN (Me = Ti, W, Cr, V, etc.) films, it is found that the surface roughness decreases with the amount of silicon addition in the films [7,8]. The surface smoothing is accompanied by the structural transformation from polycrystalline to nanocomposite and amorphous structure of the films. In this work we try the possibility of reducing surface roughness of CN_x films by adding silicon in the films. The amorphous CN_x films incorporated with various contents of silicon up to 16 at.% are prepared by reactive magnetron sputtering due to the versatility, the ease of scaling up, and the low deposition temperatures of this technique, which is desirable for practical applications. Surface morphology of the

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films is studied with scaling method based on atomic force microscopy. Surface smoothing of the CN_x films by silicon addition is observed and the mechanism is discussed in correlation with the structural evolution of the films with silicon content.

2. Experimental

The CN_x film and the films with silicon addition were deposited on commercially available Si(1 0 0) substrate in a dc closed-field unbalanced magnetron sputtering system (UDP 450, Teer Coatings Ltd.). The chamber was baked out at 600 °C (the temperature of the internal heater) and evacuated to 3×10^{-5} Torr, and then the silicon wafer and the targets were sputter cleaned for 30 min. During deposition the flow rates of Ar and N_2 were set at 12 sccm and 8 sccm, respectively. Two opposite graphite targets with current 4 A and a silicon target (current 0, 0.5, 1.0, 1.5, 2.0 A for samples S1–S5, respectively) were used. A pulsed bias voltage of −80 V was applied on substrate during the whole deposition period. The substrate rotation speed was 15 rpm, the deposition temperature was 500 °C and the working pressure was 1.3–1.0 mTorr. After deposition the samples were allowed to cool down to below 100 °C and extracted from the chamber.

Surface images of the films were taken by using an atomic force microscope (AFM) in contact mode under atmospheric condition. The scan area was $1 \times 1\ \mu m^2$ at a resolution of 256×256 pixels. Elemental composition and chemical bonding state of the films were analyzed with X-ray photoelectron spectroscopy (XPS). The chemical structure of the films was evaluated with Fourier transform infrared (FTIR) spectroscopy, and the microstructure was analyzed with field emission scanning electron microscopy (FSEM), high-resolution transmission electron microscopy (TEM) and X-ray diffraction (XRD).

3. Results

The typical AFM images of the films are shown in Fig. 1. The film S1 has big mounds with small granules of 60–80 nm in size on or between the mounds. As silicon is added into the films, the big mounds gradually disappear, and only evenly distributed small granules are observed at the surface of film S3. The surface of film S5 is rather smooth, but small granules can still be distinguished from the profile (Fig. 2(c)).

Surface morphology of the films can be qualitatively described with the scaling method. In scaling theory, for a film grown on a smooth substrate the interface width, or the surface root-mean-square (rms) roughness is predicted to be scale-dependent and has the form of $\sigma(L, t) \sim L^{\alpha} \cdot f(t/L^{\alpha/\beta})$ [9]. Here $\sigma(L, t)$ is the surface rms roughness on length scale L at time t, α and β denote roughness exponent and growth exponent, respectively, and $f(u)$ is the scaling function of the argument $u = t/L^{\alpha/\beta}$. The growing surface will gradually roughen as deposition occurs, and

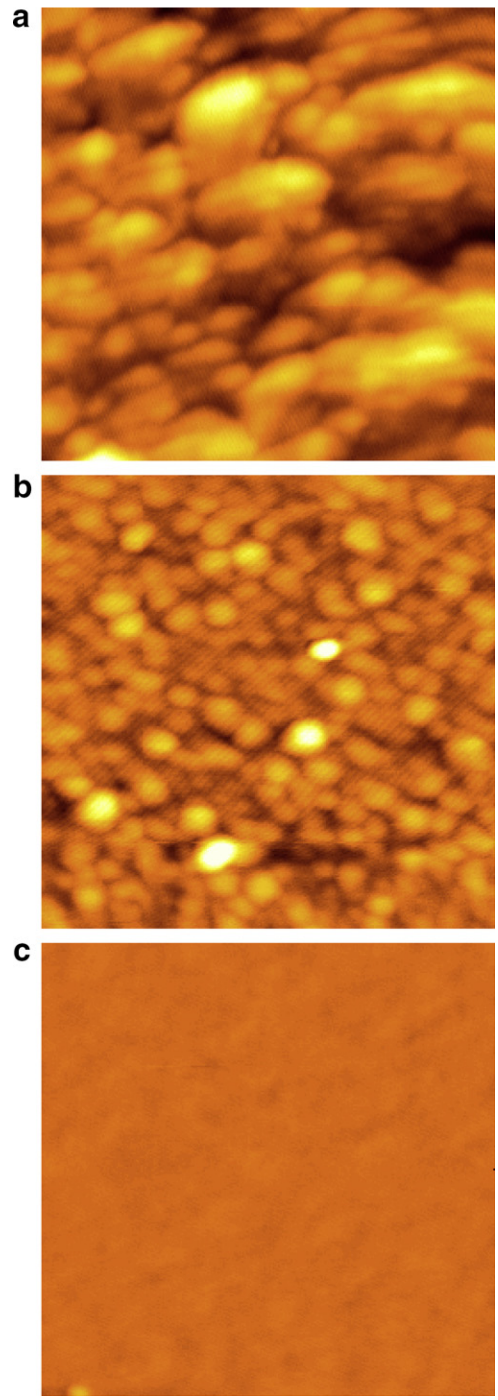

Fig. 1. AFM images of the films (a) S1, (b) S3 and (c) S5 with the scan area of $1 \times 1\ \mu m^2$.

the roughness will reach saturation over a certain time. For a fixed time, the rms roughness of the films increases with the sampling length L where $L \ll \xi$: $\sigma \sim L^{\alpha}$, and is saturated where $L \gg \xi$ (Fig. 3). Therefore, the roughness exponent α can be obtained by fitting the linear part of the σ–L plot, and the lateral correlation length ξ can be used to estimate the average half width of the mounds.

The rms roughness σ of the films decreases with the silicon target current from 3.05 nm for film S1 to 0.33 nm for