FABRICATION OF HIGH ASPECT RATIO WRINKLES BY CARBON DEPOSITION ON SOFT POLYMER

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1 Introduction

Instability of a thin film attached to a compliant substrate often leads to emergence of exquisite wrinkle patterns with length scales that depend on the system geometry and applied stresses. Mechanical instabilities, in thin films are generally treated as a nuisance in past. However, this view has changed recently with the development of pattern-controlling techniques, and the emergence of novel applications that benefit from the created patterns. These applications range from optical devices to cell templates and nanochannels for protein condensation.[1]

A common class of these techniques is based on inducing a strain mismatch between a stiff thin film and a soft substrate, causing the instability and wrinkling of the stiff film. Normally, the ratio of wrinkle amplitude/wavelength is limited to 1/10.

In this study, we created buckle patterns with high amplitude/wavelength ratio by the deposition of an amorphous carbon film on a surface of poly(dimethylsiloxane) (PDMS). Amorphous carbon films are used as a protective layer in structural systems and biomedical components, due to their low friction coefficient, wear resistance, and high elastic modulus and hardness.[2,3] We also applied glancing angle deposition (GLAD) for deposition of an amorphous carbon film on a PDMS surface. GLAD is one of a physical vapour deposition method, used to fabricate functional thin films with a columnar morphology. The application of the created morphologies range from sensors and actuators to optical filters, microfluidics, and catalysis.[4]

As an extension of this technique, we demonstrated that the amorphous carbon deposition on a pre-patterned polymeric surface allows fabrication of high aspect ratio wrinkles. Using this method, we created the patterns of two-dimensional wrinkles with a controllable wavelength that depends on the treatment time and was varied between 200 to 1400 nm in this study. In the next step, an amorphous carbon film gets deposited on the pre-patterned surface using GLAD to elevate the amplitude of the patterns.

2 Experimental methods

Wrinkle patterns with a high amplitude/wavelength ratio were fabricated with deposition of an amorphous carbon film on PDMS using GLAD. PDMS substrates were prepared by a mixture of elastomer and cross-linker in a mass ratio of 10 : 1 (Sylgard-184, Dow Corning, MI, USA). The mixture was placed in a plastic box and stirred to remove trapped air bubbles and then, cured at 80℃ for 2 h, resulting in a cross-linked PDMS network, which was cut as coupons of 20mm×20mm×3mm for the experiments.

The carbon film deposition and also the Ar ion beam treatment of PDMS and were carried out in a linear ion gun (DC 3 kV/6 kW, EN Technologies). The amorphous carbon film was deposited on flat PDMS coupons by introducing the acetylene (C2H2) into the ion gun at a flow rate of 8 sccm. During carbon deposition, the anode voltage was kept at a constant value of 1 kV and a radio frequency (r.f.) bias voltage was applied to the substrate holder at a bias voltage of -200 V. In this study, the carbon deposition time was kept between 30 s to 50 min, while the incident angle of hydrocarbon ion was varied from 0° to 75°.

The Ar ion beam irradiated sample coupons were placed in the ion beam chamber, and the chamber was evacuated to a base pressure 2×10^{5} mbar. The

distance between the ion source and the substrate holder was approximately 15 cm. Ar gas was introduced into the end-hall type ion gun to obtain Ar ions with a flow rate of 8 standard cubic centimeters per minute (sccm). The anode voltage was kept at a constant value of 1 kV with a current density 50 mA/cm^2. A radio frequency (r.f.) bias voltage was applied to the substrate holder at a bias voltage of -600 V and a corresponding current of 44 mA. The PDMS was exposed to Ar ion beam for 10 s to 50 min, leading to creation of wrinkles.

The morphology of the created patterns was measured with an atomic force microscope (AFM, XE-100, Park Systems) and a scanning electron microscope (SEM, NanoSEM, FEI Company). Raman spectroscopy analyses were performed on wrinkled amorphous carbon surfaces to investigate the ion-induced chemical changes of the surface layer. The Raman measurements were made in a backscattering geometry with a Raman spectrometer (LabRAM HR, HORIBA Jobin-Yvon Inc.) filled with a liquid-nitrogen cooled CCD detector.

3 Result and Discussion

The wavelength of the wrinkles is relatively insensitive to the deposition angle and duration and is ~750 nm. In contrast, the amplitude of the wrinkles depends on the deposition angle and duration. The wrinkles created by 50 min carbon deposition normal to the substrate surface has an average amplitude 144 nm and has the appearance of nonlinear wrinkle configurations observed in a biaxially-compressed film on a compliant substrate. The patterns formed by deposition at 45° and 75° have approximately the same wavelength, but much higher amplitudes (amplitude/wavelength ratios of ~ 2 and 2.5, respectively). Fig. 1 displays the SEM images of surface patterns created by carbon film deposition at 75° with different deposition durations, showing that the wrinkle amplitude increases for longer deposition durations. Ion or plasma treatment at an oblique angle results in formation of a porous thin film with anisotropic features that are induced by the atomic-scale shadowing, or self-shadowing.[5] At early stages of the deposition, wrinkles could emerge due to the relaxation of the strain energy in a compressively stressed thin film as shown in Fig. 1(a). For a longer deposition time, the porous structure keeps growing on the wrinkled surface, resulting in an increase in the surface amplitude as shown in Fig. 1(d).

In Fig. 2(b), we measured the amplitude/ wavelength ratio of patterns created on a PDMS surface at three different deposition incident angles as a function of the deposition time. At an incident angle 0° and 45°, the amplitude/wavelength ratio is relatively independent of the deposition time (in the range studied here, 30s–50min) and is 1/10 and 1/2, respectively. In contrast, the amplitude/wavelength ratio of the patterns created with the incident angle 75°, increases by increasing the deposition duration, resulting to an amplitude/wavelength ratio aspect ratio as high as 2.5.

For controlling the wavelength of wrinkle, we applied Ar ion beam irradiation pre-treatment. In previous study, the wavelength of wrinkle is known to be determined by mechanical property of film and substrate and thickness of deposited film.[6] Fig. 3 shows AFM profile images of three different wrinkle patterns created on a PDMS surface by Ar ion beam irradiation. The ion beam irradiation results in the formation of a thin stiff skin on the polymer surface which is ~100 times stiffer than PDMS and is under compressive stress. The morphology of the created patterns depends on the state of stress in the thin film. For the ion beam irradiation normal to the polymeric surface, the state of stress in the thin film is semi-equal biaxial and the wrinkles are semi-labyrinth shape. The wrinkle wavelength mainly depends on the film thickness, t, and the ratio of elastic moduli of thin film and substrate, E_f/E_s.[8] In Fig. 3, we can see the wrinkle wavelength versus the Ar treatment time, which was varied between 30 s and 50 min. The created patterns have a wavelength in the range of 300 nm to 1500 nm.

The ion-induced chemical changes of the surface layer were investigated by Raman spectroscopy analysis on wrinkled amorphous carbon surfaces. Fig. 4 shows the Raman spectra of a pristine PDMS, a PDMS treated by Ar ion treated for 10 min and a PDMS after amorphous carbon films deposition at 0° and 75° incident angles and with different durations. There is no significant change in Raman spectra of an Ar treated PDMS compared to a pristine PDMS. The Raman spectrum of a deposited carbon film was deconvoluted using Gaussian distribution. A linear background into two peaks located at 1365 cm^{-1} and 1535 cm^{-1} represent disordered graphite clusters with short range of

crystallinity (denoted as D peak) and graphite-like sp2 bonded carbon (denoted as G peak), respectively. In the Raman spectra, the G peak position shifts to a higher wave number for a longer amorphous carbon deposition time and also as the deposition angle is changed from 75° to 0°. This change indicates an increase in the sp2 bonded aromatic sites. The graphitization of the films is also observed as the intensity of the D peak increases and the shoulder is more pronounced. Fig. 4 shows that the intensity ratio of the D peak to the G peak (ID/IG) increases by increasing the deposition time and by decreasing the deposition angle. This suggests that the number and/or size of sp2 graphite clusters increases and the amorphous carbon film becomes more graphitic. The stress in the amorphous carbon film is known to decrease with increasing the sp2 content. So with increasing the anode voltage, the sp2 fraction increases and the stress in the amorphous carbon film decreases.

4 Conclusion

We employ glancing angle deposition (GLAD) for deposition of a high aspect ratio patterns with amorphous carbon coating on a PDMS surface. Using this method, pattern amplitudes of several nm to submicron size can be achieved by varying the carbon deposition time, allowing us to harness patterned polymers substrates for variety of application. Specifically, we can demonstrate a potential application of the high aspect wrinkles for changing the surface structures with low surface energy materials of amorphous carbon coatings, increasing the water wettability.

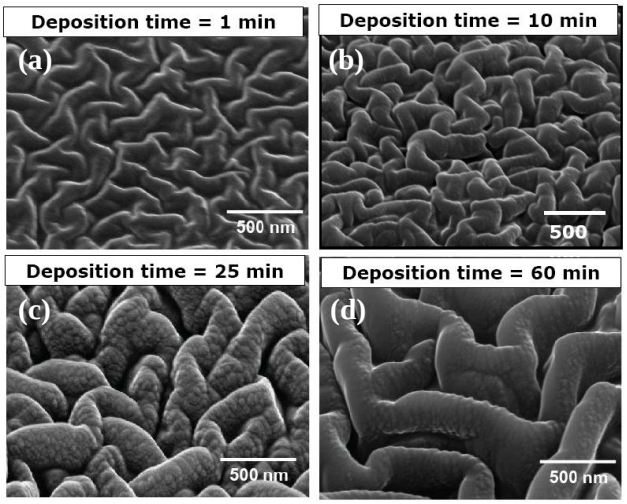

Fig.1 (a)-(d) SEM images of the PDMS surface after carbon film deposition at 75° incident angles for four different deposition durations.

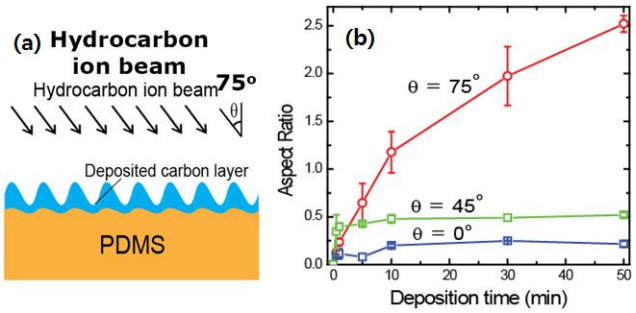

Fig.2 (a) Schematic of glancing angle carbon deposition. (b) Aspect ratio of the amplitude to wavelength for patterns created by carbon film deposition at different angles, versus the deposition time.

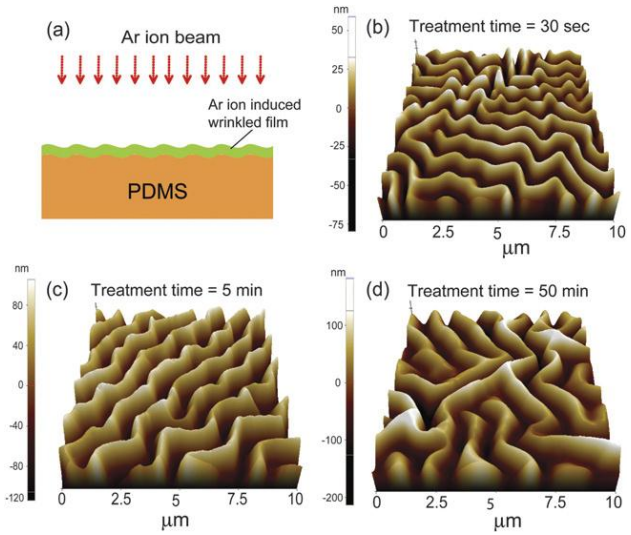

Fig. 3 Ar ion treatment of PDMS. (a) Schematic of the experiment. (b–d) AFM images of the wrinkles formed by the ion beam irradiation with different treatment times on the surface of PDMS.

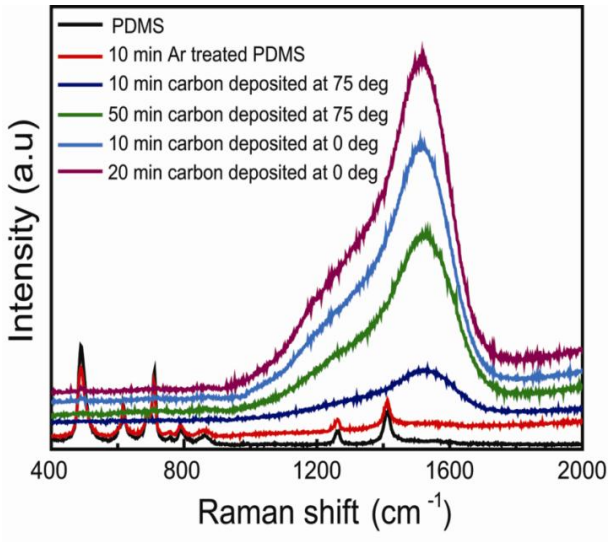

Fig. 4 Raman spectra of PDMS, Ar ion treated PDMS and PDMS with amorphous carbon films deposition at different deposition angles and durations.

References

[1] X. Jiang, S. Takayama, X. Qian, E. Ostuni, H. Wu, N. Bowden,P. LeDuc, D. E. Ingber and G. M. Whitesides, "Controlling mammalian cell spreading and cytoskeletal arrangement with conveniently fabricated continuous wavy features on poly(dimethylsiloxane).", Langmuir, Vol. 18, pp 3273–3280, 2002.

[2] R. K. Roy and K.-R. Lee, "Biomedical Applications of Diamond-Like Carbon Coatings: A Review", J. Biomed. Mater. Res., Part B, 83b, 72–84, 2007.

[3] M. Anil, S. F. Ahmed, J. W. Yi, M.-W.Moon, K.-R. Lee, Y. C. Kim, H. K. Seok and S. H. Han, "Tribological performance of hydrophilic diamond like carbon coatings on Ti-6Al-4V in biological environment", Diamond Relat. Mater., 19, 300–304, 2010.

[4] M.J. Brett and M.M. Hawkeye, "New materials at a glance", Science, Vol. 319, pp 1192-1193, 2008.

[5] J.J. Steele and M.J. Brett, "Nanostructure engineering in porous columnar thin films: recent advances", J. Mater. Sci.: Mater. Electron, Vol.18, No.4, pp 367–379, 2007.

[6] M.-W. Moon, S. H. Lee, J.-Y. Sun, K. H. Oh, A. Vaziri and J. W. Hutchinson, "Wrinkled hard skins on polymers created by focused ion beam", Proc. Natl. Acad. Sci. U. S. A., 104, 1130–1133, 2007.

[7] N. Bowden, S. Brittain, A. G. Evans, J. W. Hutchinson and G. M. Whitesides, "Spontaneous formation of ordered structures in thin films of metals supported on an elastomeric polymer.", Nature, 393, 146–149, 1998,.