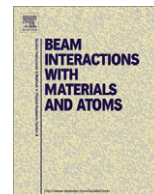


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Tailoring surface topographies of polymers by using ion beam: Recent advances and the potential applications in biomedical and tissue engineering

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ABSTRACT

Ion beam technique has recently been actively employed to create various patterns on the surface of polymers. In this paper, we highlight some of the recent advances in tailoring surface topographies of polymers by using ion beam and present a brief discussion on the potential applications in biomedical and tissue engineering.

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1. Introduction

The demand for polymeric materials has been increasing and highly functionalized polymers are much desired for wider applications to the production materials ranging from eco-friendly materials to biomaterials. Surface modification of polymers has been extensively employed to functionalize polymers by improving the surface properties such as adhesion, wetting, and biological compatibility, which can be controlled not only by the surface composition but also by the topography of the surface.

Ion beam irradiation is one of the methods actively used for the surface modification of polymers. Exposing the surface of polymers to ion beam results in the formation of various structures such as wrinkles, dots, and ripples [1–4] and we can control the features precisely by optimizing the ion beam parameters (e.g. fluence and irradiation time), which have enabled the design and fabrication of highly complex surface topographies.

In this paper, we highlight some of the recent reports on surface topographies of polymers tailored by using ion beam after introducing our basic approaches to creating patterns on the surface of polymeric substrates. We then briefly discuss the potential applications in biomedical and tissue engineering.

2. Surface patterning of polymers and the potential application in biomedical and tissue engineering

In this section, we first give a brief introduction of our experiments on the investigation of surface topographical changes of poly(dimethylsiloxane) (PDMS) substrates due to Ar ion beam irradiation. We then highlight some of the recent advances in tailoring surface topographies of polymers and discuss the potential application in biomedical and tissue engineering.

2.1. Patterns created on PDMS surface by using Ar ion beam

We investigated the effects of Ar ion beam irradiation on the surface topography of PDMS substrates. PDMS prepolymer was prepared from a mixture of silicone elastomer base and curing agent in a ratio of 10:1 by weight (Sylgard 184, Dow Corning). The prepolymer was poured into a plastic container and the air bubbles trapped were removed in a vacuum chamber. The prepolymer was then cured at 70 °C for 3 h. The PDMS was cut into pieces for the experiments and each piece was subjected to Ar ion beam under the conditions summarized in Table 1 by using an ion gun. The ion beam was normal to the sample surface. For preparing sample (a), the PDMS pieces were prestretched uniaxially by 20% with a custom-designed screw-driven stretching apparatus. The topography of the sample surfaces was analyzed by atomic force microscopy (AFM; SPM9500J3, Shimadzu Corp., Japan) in dynamic mode.

Fig. 1 shows the AFM images of the sample surfaces. The PDMS samples prestretched uniaxially by 20% formed highly-periodic ripples perpendicular to the direction of the strain, while

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Table 1

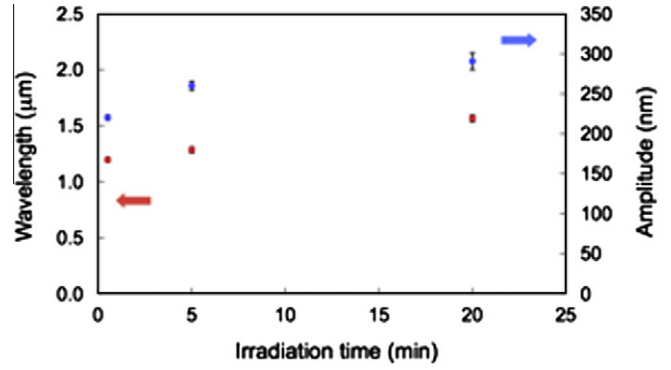
The conditions of Ar ion beam irradiation for PDMS samples.

	(a)	(b)	(c)	(d)
Ar flow rate (sccm)	8.0	12.0	12.0	12.0
Anode voltage (kV)	1.0	1.0	1.0	1.0
Bias voltage (V)	−600	−600	−600	−600
Irradiation time (min)	15	0.5	5	20
Pre strain (%)	20	0	0	0

disordered wrinkles were created on the samples unstretched prior to the ion beam irradiation. Ion beam irradiation results in the formation of thin stiff film on the polymer surface and the patterns formed on the surface depend on the state of stress in the film. For the ion beam irradiation normal to the polymer surface without prestretching, the state of stress in the film is semi-equal biaxial, which results in the formation of irregular herringbone patterns [5]. Fig. 2 shows the wavelength and amplitude of the wrinkles measured by AFM as a function of the irradiation time. The results are expressed as the mean of 4 replicates and the corresponding standard deviation. As the irradiation time increased, the wavelength and amplitude increased. The patterns created had wavelengths in the range of about 1.2–1.6 μm and amplitudes in the range of about 220–290 nm. The wavelength, λ , of the wrinkles, or buckling, of thin stiff film on compliant substrates can be expressed as equation (1), where t , E and ν are the film thickness, Young's modulus and Poisson's ratio, respectively. Subscripts s and f denote the substrate and the film, respectively [6].

$$\lambda = 4.36t \left[\frac{(1 - \nu_s^2)E_f}{(1 - \nu_f^2)E_s} \right]^{1/3} \quad (1)$$

This equation shows that an increase in Young's modulus and/or the film thickness lead to an increase in the wavelength. In this study, Young's modulus for the stiff film would be constant regardless of the irradiation time, while the film thickness would increase linearly with the irradiation time, which accounts for the increase in the wavelength with increasing irradiation time. The amplitude,

**Fig. 2.** Wavelength and amplitude of the wrinkles created on the surface of PDMS substrates as a function of the irradiation time.

A , of the wrinkles can be given by equation (2), where ε and ε_c are the applied strain and the critical strain to induce buckling, respectively [7].

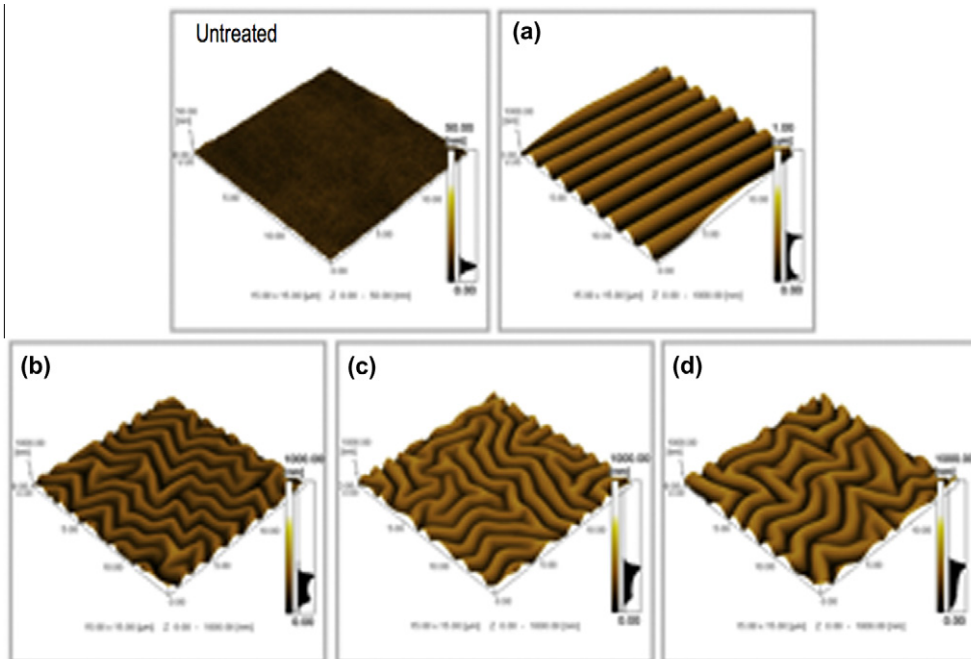
$$A = t \sqrt{\frac{\varepsilon}{\varepsilon_c} - 1} \quad (2)$$

Ahmed et al. have reported that the amount of applied strain is limited by the nature of the polymer and the amplitude of the patterns created is thus on the order of the film thickness [5].

These results demonstrate that we can control the wavelength, amplitude and surface patterns easily by prestretching the substrates and/or controlling the ion beam irradiation time.

2.2. Surface topographies of polymers tailored by using ion beam

As described above, the controls of the irradiation parameters directly affect the surface topographies of the PDMS substrates and more complicated surface topographies tailored by using ion beam have recently been reported. In this section, we introduce several researches on the creation of patterns on the surface of initially flat or pre-patterned polymer substrates.

**Fig. 1.** AFM images of PDMS sample surfaces: (a)–(d) correspond to the experimental conditions described in Table 1.

Moon et al. have developed a simple but powerful technique to create various wrinkle patterns on PDMS substrates by using focused Ga ion beam. They have reported that the surface morphology of the wrinkle patterns induced by ion beam depends primarily on the ion fluence. Moreover, the wrinkle pattern can be generated along selected paths with specified width by controlling the relative motion of the substrate and ion beam [2]. Other surface topographies such as nano-tunnels and nanofiber-like structures have been reported for poly(methyl methacrylate) (PMMA) irradiated with Ga ion beam and polypropylene (PP) with Ar ion beam [8,9].

Irradiating pre-patterned polymer surface with ion beam is an effective and powerful approach to creating more complicated surface features. Moon et al. have reported a technique to create tilted micropillars that mimics a gecko's footpad. They first fabricate straight micropillars on PDMS surface by using soft lithography and then irradiate the pillars with Ar ion beam, which caused the micropillars to tilt uniformly towards the ion beam irradiation direction, resulting in a uniform array of tilted micropillars. They have revealed that the ion beam incident angle can control the tilted angle [10]. Ahmed et al. fabricated wrinkle patterns on PDMS surface by utilizing Ar ion beam irradiation and coating amorphous carbon films [5]. According to their report, the amorphous carbon deposition did not change the wavelength of the pre-patterned surface considerably, while elevating the surface amplitude. This technique is attractive not only because of the structural evolution but also because of the deposition of amorphous carbon films. Amorphous carbon, or diamond-like carbon (DLC), has attracted much attention as a coating material for biomedical devices owing to the outstanding properties [11], and we have reported improved non-thrombogenic properties of the substrates due to DLC coatings [12–15]. Therefore, the wrinkled surface combined with amorphous carbon films would possess biological compatibility and may have the potential for a vast range of applications, for instance, biomedical devices and artificial organs.

2.3. Potential application in tissue engineering

Tissue engineering is an interdisciplinary field that applies the principles of engineering and life sciences toward the development of biological substitutes that restore, maintain, or improve tissue function or a whole organ [16]. Engineering substrates to induce desired cell function has become an important component of scaffold design for tissue-engineering applications because the surface topography of the scaffolds has proven to affect basic cell function in almost all types of mammalian cells [17]. Natural tissues or organs are nanometer in dimension and cells directly interact with nanostructured extracellular matrix (ECM) and the biomimetic features of nanomaterials would thus play a key role in stimulating cell growth as well as guide tissue regeneration. Recent advances in the ion beam techniques for creating various patterns on the surface of polymers can enable the design and fabrication of scalable scaffolding materials mimicking the structural cues present in the ECM environment, which will not only give an insight into how cells function within our bodies, but will also contribute to the development of advanced tissue engineering scaffolds.

3. Summary and future outlook

We have highlighted some of the surface topographies of polymers created by using ion beam technique. Various surface topographies such as wrinkles, dots and ripples can be easily created by the technique and the control of the ion beam irradiation parameters directly affects the surface topographies. The interaction of mammalian cells with nanoscale topography has proven to be an important signaling modality in controlling cell function and engi-

neering substrates to induce desired cell function has become an important component of scaffold design for tissue-engineering applications. The ion beam technique with simple but proper control of the parameters for creating various surface topographies on the surface of polymers should thus be highly applicable to the design and fabrication of advanced tissue engineering scaffolds.

Surface modification using ion beam irradiation has a vast range of applications; therefore, it is crucial for materials scientists, biologists and medical doctors to firmly collaborate and seek to understand how the local interactions between cells and their surrounding microenvironment can regulate cellular behavior in order to develop highly-functionalized scaffolds for tissue engineering applications.

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