# Fabrication and assembly of nanowrinkle patterns on metallic surface: a nonlithography method for nano fabrication

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## ABSTRACT

Motivated by wrinkles, which are ubiquitous in nature, artificial patterns with micro periods were also fabricated in stiff/soft bilayer. Since its great importance in both fundamental research and practical use, ordered periodic nanostructures fabricated by wrinkling has fascinated researchers. In this paper, the wrinkle patterns with periods from micro- to nano-scale (sub 500nm) were fabricated by choosing the appropriate metal film and optimizing the film thicknesses. The influence of metal film morphology on wrinkle pattern was studied, which is seldom mentioned in existing works. Furthermore, the wrinkle patterns were assembled by the prefabricated structures produced via nanoimprint, deposition with masks and laser scanning. Our research results show that the wrinkling of polymer/metal bilayer is a potential nano fabrication method combining conventional bottom-up with top-down nanofabricating technique.

***Keywords***: wrinkle, assembly, nano fabrication, nonlithography

## 1 INTRODUCTION

With the development of modern technology, the fabrication of periodic microstructures has been attracting persistent attention [1]. Although kinds of techniques such as contact printing techniques[2, 3], electron beam lithography (EBL)[4, 5], focused ion beam (FIB) processing[6] have been extensively pursued to fabricate nanoscale features, novel techniques is still developed to satisfy increasing demands of low cost, large area nanofabrication. Motivated by wrinkle, the ubiquitous phenomena in nature, spontaneous formation of wrinkle patterns has been utilized to fabricate periodic microstructure. Various applications of periodic structures via wrinkling, such as flexible electronics [7, 8], tunable diffraction grating [9], biocompatible cell and particle alignment [10], advanced metrology methods [11-13], have been developed.

The wrinkle pattern has a well defined wavelength, which is approximately proportional to the thickness of buckled film. Thus a periodical structure with wavelength on micro/nano scale can be fabricated by wrinkling of thin films. Compare to the existing micro/nano fabrication method, the fabrication method via wrinkling has the follow advantages. First, the wrinkle can be simply generated by thermal stress, stretching and swelling. Second, the wrinkle wavelength can be controlled by the film thickness and materials properties. Last, the wrinkle can be realized in a large area easily. However, to our best knowledge, the nano fabrication via wrinkling has not been realized yet, because there are problems needed to be solved.

The larger wrinkle wavelength is the first problem for nanofabrication. The previous works have significantly reduced the wavelength from macroscopic scale to micro scale [14-18]. Recently, the wrinkle wavelength has been reduced to submicron scale (ca. 500 nm) on metallic surface via thermal wrinkling [19, 20]. Unfortunately, the smaller wrinkle pattern on metallic surface has not been reported yet, which hinders the application of wrinkle from micron scale to nano scale.

Another barrier of nanofabrication via wrinkling is the randomness of wrinkle pattern. The isotropic stress induced by annealing, swelling etc. usually produce a chaos and complicated patterns, which is hard to utilize and most treated as a nuisance. The ordered wrinkle patterns are desired for device use. The effective and low cost assembly method is still desired urgently.

Not confined to a technique issue, nano fabrication via wrinkling makes the conventional theory of wrinkle phenomena face a great challenge. The small wavelength demand an ultra thin metal film, which shows a discontinuous morphology composed of grains. The influence of metal film morphology on wrinkle pattern is seldom mentioned.

As a consequence, the wrinkling method is a promising nanofabrication, but there are still problems need to be resolved. In this paper, we have fabricated the wrinkle patterns with periods from micro- to nano-scale (sub 500nm) by material selection and film thickness optimization. Several assembly methods have been proposed to obtain ordered wrinkle patterns. A brief theory analysis has been given based on conventional wrinkle models.

## 2 EXPERIMENTAL DETAILS

### 2.1 Sample preparation and wrinkle process

The wrinkle experiments were preformed on the polymer/metal bilayer system. The polystyrene (PS) was chose to be the polymer layer due to its mechanic property and inexpensiveness. A toluene solution of the PS (Mw=100,000) was spin-coated onto a cleaned silicone wafer, and then was annealed at 60 °C for 12 h to remove the residual solvent and to relieve the stress induced by spin-coating. The PS films were controlled to various thicknesses by adjusting the solution concentration or/and the spin-coating speed and determined by profilegraph (Dektak 150, Veeco). Various kinds of metal were deposited on PS film by RF magnetron sputtering (ULVAC, ACS-4000-C4). The bilayer system was heated to a temperature which is higher than the glass transition temperature of PS (100 ℃) in a vacuum oven. The thermal stress during the heating process generated the wrinkle patterns on the sample surfaces.

## 2.2 Characterization of wrinkle patterns

The surface morphology of wrinkled sample was examined by optical microscopy (OM, OLYMPUS BX51), field emission scanning electron microscopy scanning electron microscopy (SEM, HITACHI S4800), and atomic force microscopy (AFM). The AFM images were all acquired in the tapping mode with a VEECO Dimensions 3100 instrument and a Nanoscope Ⅳa controller. All measurements by AFM were performed at ambient conditions in an acoustic damping box. The software packages 5r30 and 6r13 were used for data analysis.

# 3 RESULTS AND DISCUSSIONS

## 3.1 The wavelength reduced by optimizing material parameters

A simplified prediction of wrinkle wavelength has been given as $\lambda \sim t_m(E_m/E_p)^{1/3}$. Most of achievements in wrinkle wavelengths are based on thinning the films. And the submicron metallic wrinkle pattern has been successfully fabricated based on PS/Au bilayer by thermal wrinkling However the wrinkle wavelength is about 500 nm[19] ,while the thickness of Au film has reached to 5 nm, which is nearly the lower limit of continuous film, and the PS film is about 120 nm. The thinner PS film will cause the sharply increase of the critical stress to wrinkle. Thus reducing the thickness for smaller wrinkle pattern is effective but hard to be improved. As another influence factor, the lower modulus of metal film can also lead to smaller wavelength in a lower level than film thickness. In Fig. 1, the wrinkle patterns of some soft metal supported on PS film were fabricated by thermal wrinkling, which verified that thermal wrinkling is a versatile microstructure fabrication on various metals.

Among kinds of soft metal, we choose Sn as the metal film due to its low modulus (41GPa for bulk Sn) and high quality of film. Fig 2 shows the wrinkle patterns of Sn with different thickness on 56 nm PS film. The thickness of Sn film is controlled by the deposited time. It is obvious the wrinkle have an increasing wavelength as the increase of deposited time. It should be noted that the Sn film not only affects the wrinkle wavelength, but also the morphology of the wrinkle. For an excessively thick Sn film, such as deposited for 300, 400, 500 s, the wrinkle pattern have an island-like structure with low amplitudes, because the thick film has a high stiffness. However, for an excessively thin Sn film, the wrinkle gets hazy and looses its periodicity, because the poor continuity of .the film. The Sn film deposited for 100 s, has a best labyrinth pattern and smallest wavelength. The thickness is determined to be about 5 nm by AFM.

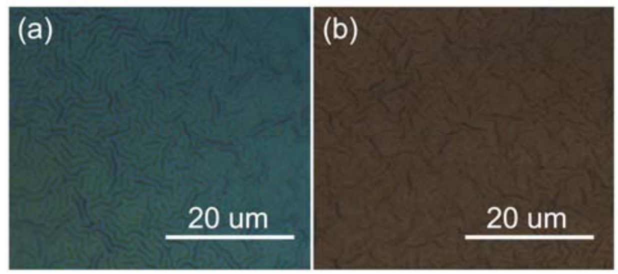


Figure 1: OM images of wrinkles of 20 nm Bi (a) and Sn (b) on 120 nm PS film. The wrinkles were fabricated by annealing the samples at 120 °C for 2 h.

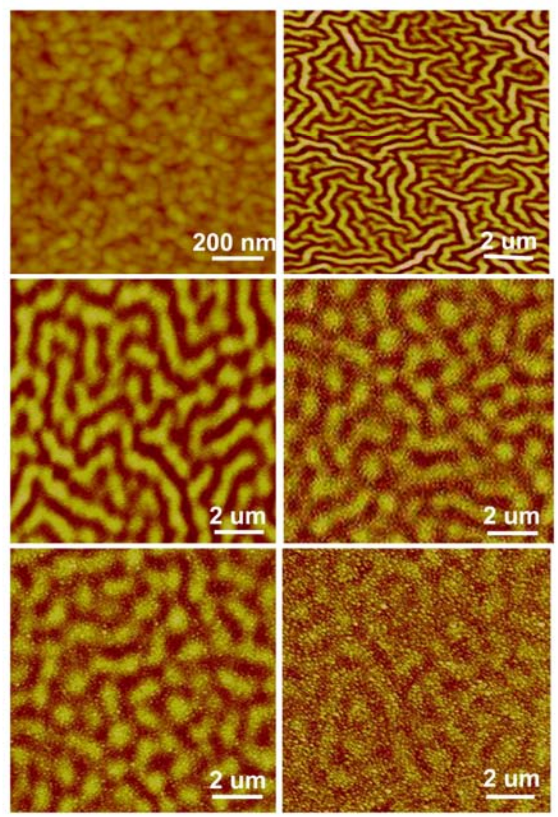


Figure 2: Wrinkles of different Sn film on 56 nm PS. The Sn films are deposited for 60(a), 100(b), 200(c), 300(d), 400(e) and 500(f) s. The wrinkles were fabricated by annealing the samples at 120 °C for 2 h. The color scale is 50 μm.

Besides the metal film, the polymer film is also seriously affects the wrinkle wavelength, especially when the polymer film is comparable to the metal film. Fig 3 shows the wrinkle patterns of 5 nm Sn film supported on the PS films with different thicknesses. A downtrend of wrinkle wavelength is obvious as decreasing the thickness of PS film. Thus wrinkle wavelength has been reduced to below 200 nm, which is much lower than existing reported metallic wrinkle wavelength, by using the appropriate metal and optimizing the thicknesses of both metal and polymer films.

## 3.2 The assembly method of wrinkle patterns

Reducing the wavelength is the first step of nanofabrication by wrinkling. The controllability of wrinkle pattern is important and necessary. Many methods have been proposed to assemble the wrinkle [17, 18].Here, we present some novel methods to obtain ordered wrinkle pattern. In Fig. 4, some ordered wrinkle patterns have been fabricated via different methods. All these methods are prefabricating patterned structures before annealing. The wrinkle pattern will have some favored direction related to the prefabricated structures. Fig 4(a) (b) show ordered wrinkle patterns assembled via thermal nano-imprint. A template is needed to imprint structures on PS films. The wrinkles are assembled to be perpendicular to the edges of prefabricated structures, because the stress relaxation perpendicular to the edges. The wrinkle pattern in Fig 4(c) is obtained via selective area film deposition. After a PS/Sn bilayer is produced, the left part is covered by a mask. A continuative Sn film deposition will cause the different thickness of covered and uncovered parts. The edge of thicker part will produce a pinning effect, which cause the increase of perpendicular stress in the adjacent area. An ordered wrinkle pattern paralleled to the edges appears. Another wrinkle assembly via laser scanning is shown in Fig 4(d). The ablation of Sn film via laser scanning produces break of films. The break will relieve the perpendicular stress, thus the wrinkles are perpendicular to the scanned line.

All these methods have been proved to be effective assembly method, although there are many defects. The defects come from the sensitiveness of stress distribution, the defects of prefabricated structures and the geometrical limit. Development of novel, simple assembly method is still needed

## 3.3 The influence of metal film morphology on wrinkle pattern

The conventional wrinkling theory is based on a model, in which the metal film is treated as a flat, continuous layer. When the metal film is limited to a very thin thickness due to the demands of small wavelength, the detailed morphology of film is a network of grains. The influence of film morphology on wrinkle pattern can not be studied from the conventional model. Here we have studied the wrinkle on the bilayers with same thickness but different morphology.

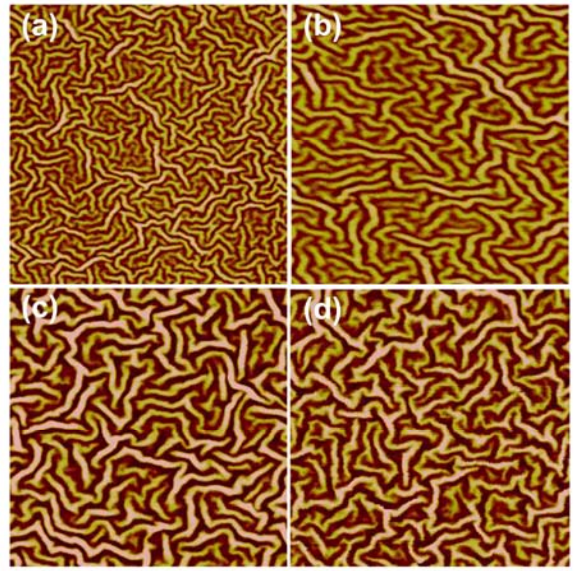


Figure 3: AFM images (5 μm×5 μm) of wrinkles on 5 nm Sn film supported on different PS films. The thicknesses of PS films are 23 nm (a), 56 nm (b), 71 nm (c), 165 nm (d). The color scale is 50 μm.

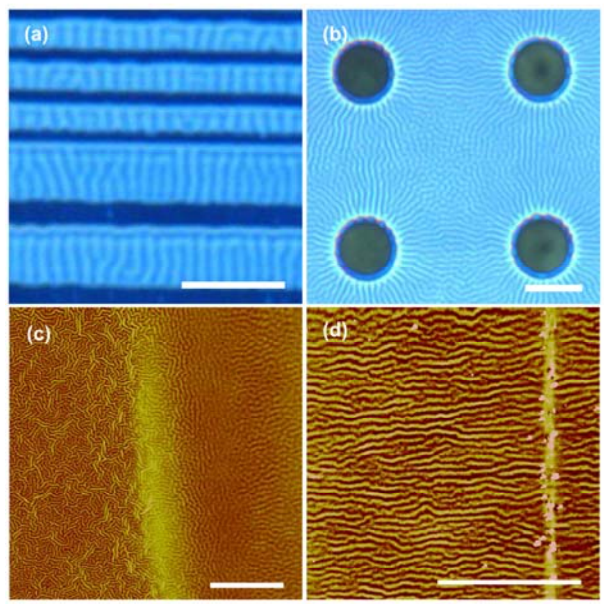


Figure 4: OM images (a, b) and AFM images (c, d) of wrinkle patterns assembled by various method. The scale bar is 5 μm.

The 20 nm Sn film with different morphology was fabricated by once 400 s (Fig. 5(b)), twice 200 s (Fig. 5(d)), and four 100 s (Fig. 5(f)) deposition respectively [21]. The SEM images show that the four 100 s deposited film has the finest and homogenous grains while the 400 s deposited film has the largest and inhomogeneous grains. The wrinkle patterns of these 20 nm Sn films supported on 310 nm PS are shown in Figs. 5(a), 5(c) and 5(e), respectively. All these wrinkles have no significant change in wavelength because the same thickness and materials of films, while the amplitude is different. The film with finest and homogenous grains is most likely to a continuous layer. Thus the corresponding wrinkle is clearest and has largest amplitude. However, the multi-times deposited films have both larger grains and fine grains, which damaged the uniformity. The existing of giant grains will bury the wrinkle structure, thus make the wrinkle hazy and reduce the amplitudes. In order to obtain a clear, well developed wrinkle pattern, the thin film with fine and homogenous morphology is preferred.

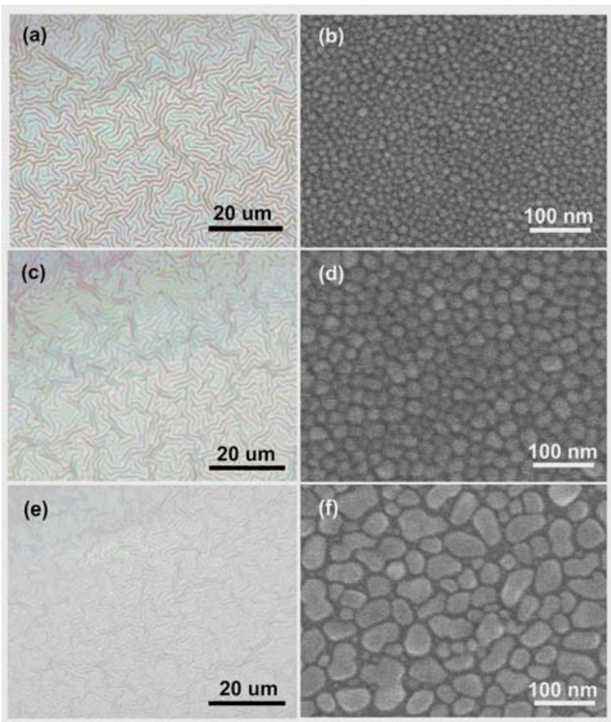


Fig. 5: The influence of film morphology on wrinkle patterns: (a), (c), (e) wrinkle patterns of 20 nm Sn film on 310 nm PS film after heating at 120 °C for 4 h. (b), (d), (f), the film morphology of Sn film in (a), (c),(e) respectively.

## 4 SUMMARY

In summary, we have fabricated the wrinkle patterns with periods from micro to nano scale (sub 500nm) by choosing the appropriate metal film and optimizing the film thicknesses. Various methods of wrinkle assembly have been presented and show its effect in controlling the winkle direction. The controllability of wrinkles gives possibility of nanofabrication via wrinkling, although many efforts are still needed. Furthermore the influence of film morphology on wrinkle pattern has been studied, which indicated a homogenous thin film with fine grains is preferred for high quality wrinkle pattern.

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