

이중층 박막에서의 응력 유도 패턴의 변화: 스피노달 좌굴현상

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Evolution of Stress-Driven Pattern in Thin Bilayer Films: Spinodal Wrinkling

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Introduction

Wrinkle formation in layered systems is a well known phenomenon and believed to take place spontaneously by an abrupt compressive stress, which is originated from the misfit strain is the driving force that is caused by a mismatch in thermal expansion coefficient.

The bilayer system being considered is a thin polymer layer capped with a thin metal layer. The stress on the metal layer is generated upon heating the bilayer, which is tensile. As such, the metal surface would fracture once the stress exceeds its critical value if a simple expansion occurs in the polymer layer due to its larger thermal expansion coefficient. Our experimental results show, however, that an isotropically wrinkled surface results instead of fractured surface, indicating that the viscoelastic property of polymer induces an instability and makes the polymer deform in vertical direction in relieving thermal stress.

Experimental Method

Bilayers of aluminum on polystyrene (PS) were used in our experiments. Typically, a toluene solution of PS (high molecular weight: $M_n = 1,340,000$, $M_w/M_n = 1.05$) was spin-coated onto a silicon substrate, on which aluminum was thermally deposited to a desired thickness. For wrinkle formation, the prepared samples were placed in a constant-temperature oven and annealed for a period of time and then the temporal evolution of wavy surface structure by atomic force microscopy (AFM) in the contact mode. Most of the experiments were carried out at 140°C , well above the glass transition temperature of about 105°C of the high molecular weight PS.

Temporal evolution of the surface pattern thus obtained experimentally is shown in Figure 1. There are two distinct transitions in both sets regardless of the wave size under isothermal condition. One is the transition from an island-like to a labyrinthine pattern as apparent in going from Fig. 1(a) to 1(b) in Set I and Fig. 1(g) to 1(h) in Set II. The formation of the island-like structure is relatively fast,

usually taking place in the first 3 minutes of annealing time. The evolution of the labyrinthine pattern to a more ordered structure takes a long time, usually more than a few days. Whether the pattern is island-like or labyrinth, this early stage, which is to be called Stage I, is characterized by the constancy of the dominant wave number of maximum intensity. The other transition is marked by the appearance of a second wave, as typified in the Fast Fourier Transforms of Fig. 1(d) and 1(i), i. e. the emergence of a second ring or a larger wave than the first in Stage I. As time progresses, the larger wave starts exerting itself and becomes dominant over the initial wave. This period is to be called Stage II.

Results and Analysis

The transition from an island-like to a labyrinthine pattern is detailed in Fig. 2. The island-like pattern is seen to evolve to a fully-developed labyrinthine pattern in about one day. The sectional data and mean roughness value in the insets show that wave amplifies continuously, while the wavelength remains the same. The facts that waves grow with time but increase only in the magnitude, which is strain in wrinkling, are similar to those found in the early stage of spinodal decomposition [1].

The constant intrinsic wavelength λ for Stage I can be determined in an a priori manner [2]. The free energy per unit area of the metal/polymer bilayer system is given by

$$F(q) = \left(\frac{E_m q^2 t_m^3}{12(1-\nu_m^2)} + \frac{E_p}{q^4 t_p^3} + \frac{2E_p}{3q} \right) \frac{(\varepsilon q)^2}{4} \quad (1)$$

where t is the thickness, E is Young's modulus, the subscripts m and p are for the metal and the polymer, respectively, q is the wave number, ε is the amplitude of the wrinkling wave, and ν_m is the Poisson ratio of the metal. The characteristic wavelength is determined by minimizing with respect to wave number the system free energy of the bilayer. The result predicts well the wavelength dependence on thickness and temperature variations. By the time a labyrinthine pattern is completed in the early stage, a larger wave emerges, signaling the beginning of Stage II. The emergence of a second peak means that a new wavelength parameter intervenes and interacts with the initial wavelength. Once the second maximum peak emerges after about 36~48 hrs of annealing, the larger waves become dominant and get to grow with time.

An interesting finding in this work is that the strain of the metal layer remains constant even with increasing wavelength once the second larger wave emerges. It is very difficult to measure the strain of a thin metal layer with a direct method. Instead, the surface area of the wrinkled surface was measured by AFM to calculate the strain indirectly. The change of the strain with time is shown in Fig. 3 for both stages. The plots show that in Stage I, the strain increases with time but then becomes nearly constant when Stage II starts. The facts that no more stretching of metal takes place and the strain is independent of time in Stage II suggest that the stress relaxation lies in the polymer layer.

For an analysis of Stage II, we utilize the viscous property of polymer. The dynamic equation of

motion for the bilayer can be expressed as follows: [3]

$$\frac{\partial}{\partial t} h(x, t) = C \frac{\partial^2 P}{\partial x^2} = C \frac{\partial^2}{\partial x^2} \left(\frac{E_m t_m^3}{12(1-\nu^2)} \frac{\partial^4 h}{\partial x^4} - \gamma \frac{\partial^2 h}{\partial x^2} \right) \quad (2)$$

where h is the film thickness, x is the lateral coordinate, C is the constant that is dependent on the flow profile and the viscosity, P is the pressure, γ is the interfacial tension. For a small fluctuation of the film thickness, this relationship leads to a stability condition that the wave number approach zero for the fastest growing wave, which means that the wavelength should continuously grow with time without bound. However, as the polymer layer thickness is finite, the wavy pattern becomes “pinned” after about 200~280 hours of annealing. Therefore, the resulting wavelength is larger for thicker polymer layer. Figure 4 shows the wave number plotted against time. It is seen that the wave number is inversely proportional to time. It is notable that this growth rate dependence is identical with that found in the late coarsening stage of spinodal decomposition [4].

Discussion and Summary

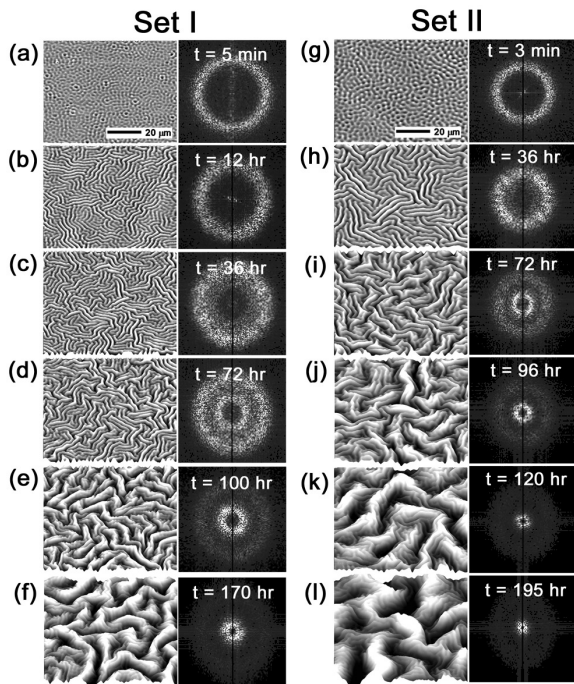
A discussion is on the similarities between the spinodal wrinkling in buckled bilayers and the spinodal decomposition in polymer blends. The initiation is by an instability in both, the former due to a thermomechanical instability that leads to a deflection wave due to a surface deformation and the latter due to a thermodynamic one that leads to a composition wave due to a phase separation. With the strain as the magnitude of wave in wrinkling, there is one to one correspondence between the stages of the wrinkling and those of the decomposition. In both cases, the wavelength is constant but the magnitude increases with time in the early stage. In the late stage, the wavelength increases with time but the magnitude stays constant. In the spinodal decomposition, the magnitude keeps increasing but eventually reaches a saturation value that corresponds to the maximum composition gradient. While the driving force in the decomposition is composition gradient, it is stress in the wrinkling. In the wrinkling, the magnitude also keeps increasing but eventually reaches a saturation value that corresponds to the maximum stress. The saturation corresponding to the maximum driving force marks the beginning of the late stage in both cases. The mechanism involved in the growth of the wavelength is coarsening in both cases. The coarsening in spinodal decomposition is viscosity-controlled and so is the coarsening in spinodal wrinkling. Therefore, the exponent of the time dependence of the wavelength growth is unity for both spinodal decomposition and spinodal wrinkling.

In summary, spinodal wrinkling can be characterized as one in which the wavelength remains constant and the strain increases with time in Stage I (elasticity-induced wave), but the strain remains constant in Stage II (viscosity-induced wave) while the wavelength increases with time [5].

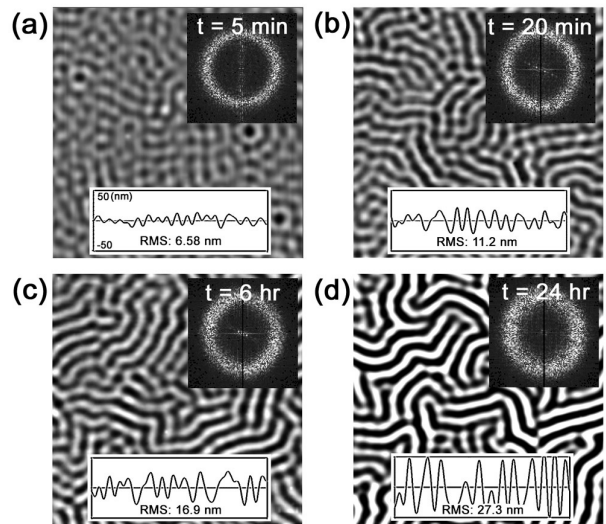
References

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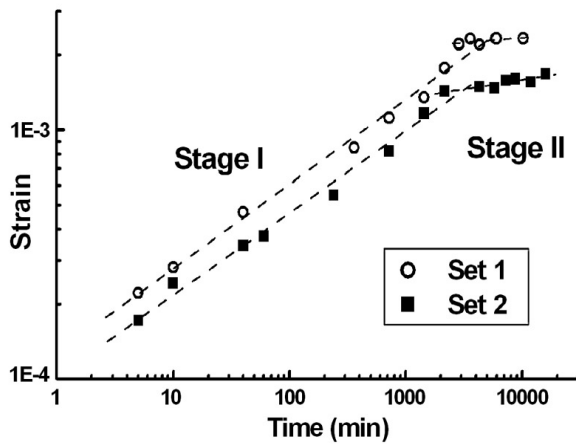
Figures



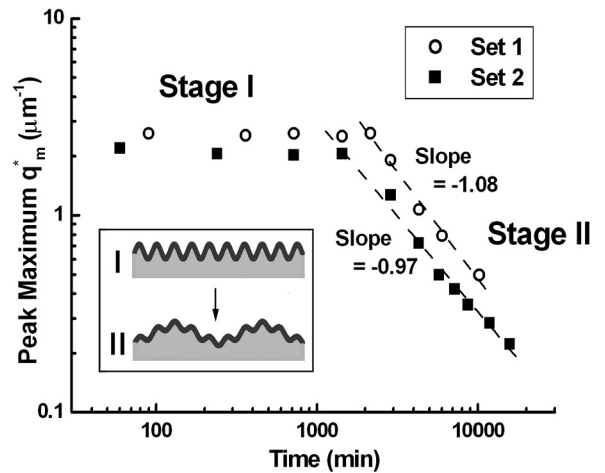
<Fig. 1> AFM images of temporal evolution of stress-driven surface wavy patterns (80 μm × 80 μm).



<Fig. 2> AFM images of initial stage of wave development (40 μm × 40 μm).



<Fig. 3> Strain-time relation of metal layer.



<Fig. 4> Dominant wave number-time relation in Stage I and Stage II.