Electronic Supplementary Information

Cumulative energy analysis of thermally-induced surface wrinkling of heterogeneously multilayered thin films

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Measurement of glass transition temperature of P4VP layer using ellipsometry

When the volume of polymer is measured during heating the polymer at constant heating rate, a point that volume begin to increase sharply can appear. This point can be regarded as the glass transition temperature (T_g), since the thermal expansion coefficient changes at T_g of polymer. Based on this principle, T_g of polymer can be determined and there have been a number of studies on the characterization of T_g. Since the T_g of thin polymer film is varied with the film thickness, we measured T_g of thin P4VP layer (thickness of 60 nm) using ellipsometry and the results are presented in Fig S1, in which T_g of 60 nm-thick P4VP layer is estimated as 148℃. This value is higher than T_g of P4VP in a bulk phase (142℃), because the affinity interaction between the P4VP and the Al layer is highly strong.

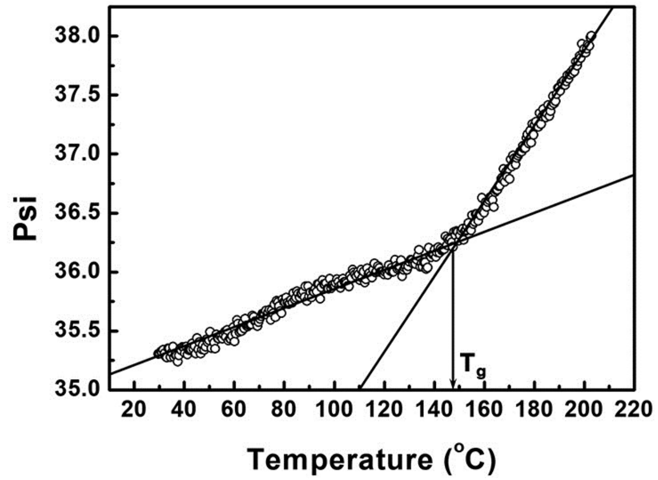

Fig. S1. Ellipsometric parameter (Ψ) measurement of thin P4VP film (60 nm) in a temperature range of 30 – 200℃

Mathematical expression for bending free energy of a single layer

When the system being deformed is regarded as an isotropic body, free energy of deformation can be given by:[1]

$$F = \mu \left(u_{ik} - \frac{1}{3} \delta_{ik} u_{ll} \right)^2 + \frac{1}{2} \kappa u_{ll}^2 \qquad (1)$$

where strain tensor $u_{ik} = \delta_{ik} \times const.$, μ is shear modulus and κ is bulk modulus. Especially, if the strain tensor is constant throughout the body (homogeneous deformation), then the free energy expression for the deformation is described as:

$$F=\frac{E}{2(1+\upsilon)}\left(u_{ik}^{2}+\frac{\upsilon}{1-2\upsilon}u_{ll}^{2}\right) \tag{2}$$

where E is elastic modulus, and υ is poisson's ratio. Now we consider the bending deformation of layer as shown in Fig. S2, here, the strain tensor term can be given by,

$$u_{xx}=-z\frac{\partial^{2}\varsigma}{\partial x^{2}},\ u_{yy}=-z\frac{\partial^{2}\varsigma}{\partial y^{2}},\ u_{xy}=-z\frac{\partial^{2}\varsigma}{\partial x\partial y},\ u_{xz}=u_{yz}=0,\ u_{zz}=\frac{\upsilon}{1-\upsilon}z\left(\frac{\partial^{2}\varsigma}{\partial x^{2}}+\frac{\partial^{2}\varsigma}{\partial y^{2}}\right) \tag{3}$$

where ς is vertical displacement of a point on the neutral surface.

Then, the free energy of a single layer bending per unit volume is calculated from combining Eq. (2) and (3).

$$F=z^{2}\frac{E}{1+\upsilon}\left\{\frac{1}{2(1-\upsilon)}\left(\frac{\partial^{2}\varsigma}{\partial x^{2}}+\frac{\partial^{2}\varsigma}{\partial y^{2}}\right)^{2}+\left[\left(\frac{\partial^{2}\varsigma}{\partial x\partial y}\right)^{2}-\frac{\partial^{2}\varsigma}{\partial x^{2}}\frac{\partial^{2}\varsigma}{\partial y^{2}}\right]\right\} \tag{4}$$

Because Eq. (4) is free energy of the unit volume, the total free energy to describe the bending deformation of a single layer can be calculated by integrating Eq. (4) over the entire volume. Although the boundaries for x and y axes are unjustified (i.e. infinite surface), z axis is readily defined as the layer thickness. Therefore, Eq. (4) can be integrated over z from $-0.5t$ to $+0.5t$ (t is the thickness of layer). As a result, the obtained form for the bending free energy is given by:

$$F=\frac{Et^{3}}{24(1-\upsilon^{2})}\iint\left\{\left(\frac{\partial^{2}\varsigma}{\partial x^{2}}+\frac{\partial^{2}\varsigma}{\partial y^{2}}\right)^{2}+2(1-\upsilon)\left[\left(\frac{\partial^{2}\varsigma}{\partial x\partial y}\right)^{2}-\frac{\partial^{2}\varsigma}{\partial x^{2}}\frac{\partial^{2}\varsigma}{\partial y^{2}}\right]\right\}dxdy \tag{5}$$

where the displacement of ς is shown as sinusoidal function ($\varsigma=\varepsilon\cos kx$). Finally, by combining equation (5) and (6), the bending free energy per area is derived.[2]

$$\frac{F_{bending}}{Area} = \frac{Et^3}{48(1-\upsilon^2)}\varepsilon^2 k^4 \tag{6}$$

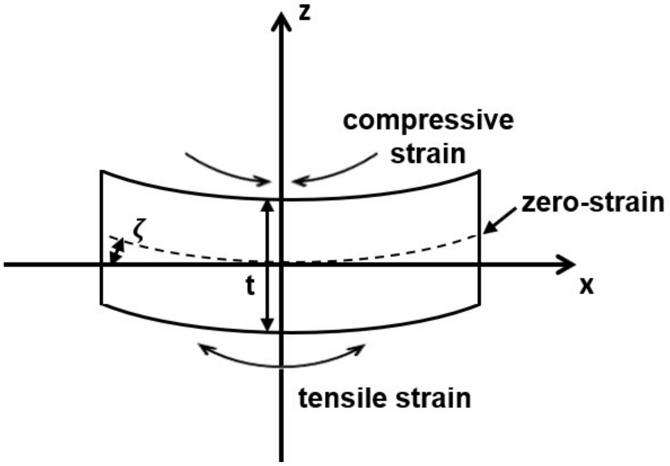

Fig. S2. Schematic illustration of bending deformation for a single layer

As illustrated in Fig S2, when bending deformation is upwardly occurred in a single layer, both compressive and tensile strains are applied to upper and lower sides of the layer, respectively, resulting in a generation of strain distribution along *z*-axis. The strain tensor term which is required for deriving the bending energy expression is determined by this strain distribution. Therefore, for heterogeneously multilayered systems, cumulative approach with considering individually divided layers can correctly reflect the strain distribution for each layer. On the other hand, if a homogeneous single layer is interpreted with cumulative approach, for which the homogeneous film is regarded as a stack of thin divided sub-layers, the sum of compressive strain at the upper side and tensile strain at the lower side is significantly falsely underestimated as compared to actual deformation. Therefore, to avoid this contradictory case in a model, a consideration for the individually divided sub-layers should be placed on heterogeneously multilayered films consisting of elastically highly distinguishable species.

References

1. L. D. Landau, E. M. Lifshitz, *Theory of Elasticity*, Pergamon, NY, 3rd edn, 1986.

2. J. Groenewold, *Physica A*, 2001, **298**, 32-45.