Graphene



# Preventing Thin Film Dewetting via Graphene Capping

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A monolayer 2D capping layer with high Young's modulus is shown to be able to effectively suppress the dewetting of underlying thin films of small organic semiconductor molecule, polymer, and polycrystalline metal, respectively. To verify the universality of this capping layer approach, the dewetting experiments are performed for single-layer graphene transferred onto polystyrene (PS), semiconducting thienoazacoronene (EH-TAC), gold, and also MoS<sub>2</sub> on PS. Thermodynamic modeling indicates that the exceptionally high Young's modulus and surface conformity of 2D capping layers such as graphene and MoS<sub>2</sub> substantially suppress surface fluctuations and thus dewetting. As long as the uncovered area is smaller than the fluctuation wavelength of the thin film in a dewetting process via spinodal decomposition, the dewetting should be suppressed. The 2D monolayer-capping approach opens up exciting new possibilities to enhance the thermal stability and expands the processing parameters for thin film materials without significantly altering their physical properties.

Thin film applications are often impeded by film rupture and dewetting during thermal and chemical processing.<sup>[1–13]</sup> Conventional approaches to suppress dewetting have mainly focused on substrate modification to tune the interfacial energy,<sup>[14,15]</sup> improvement of film stability via additives,<sup>[16,17]</sup> and application of capping layers.<sup>[18]</sup> For example, the use of nanofillers to suppress dewetting by mechanically strengthening films has been studied extensively.<sup>[19–22]</sup> The use of capping materials such as metals, oxides, and polymers has been observed to modify dewetting behavior with certain success.<sup>[23,24]</sup> While

these strategies can considerably improve the stability of thin films, it is also desirable to have approaches that can be applicable to different film/substrate systems without causing substantial changes in the functional properties of the substrate and/ or thin film.

Here we report a simple, facile strategy whereby transferring of a single layer of 2D material such as graphene or MoS<sub>2</sub> onto a film surface completely eliminates dewetting in thin films of organic semiconductor small molecules, polymer, and metal, respectively. Thermodynamic modeling indicates that dewetting is suppressed by the exceptionally high Young's modulus and surface conformity of 2D sheets that reduce surface fluctuations. Furthermore, for polymer thin films, as long as the defects in a graphene sheet are smaller than the fluctuation wavelength,

this graphene-capping approach can effectively enhance the thermal stability and expand the processing parameters for thin film materials without significantly altering their physical properties.

Graphene sheets were prepared through chemical vapor deposition (CVD) growth on copper foil<sup>[25]</sup> and subsequently transferred onto thin films to cover large (>100  $\mu$ m) areas (methods detailed in the Supporting Information). Figure 1a shows the optical image of an 18 nm polystyrene (PS) film on an oxidized silicon substrate that has a monolayer graphene layer on top of

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**Figure 1.** Polystyrene (PS) thin films are stabilized against thermal dewetting when covered by graphene (Gr). a,b) Optical microscopy images of a PS thin film (18.1  $\pm$  0.2 nm in thickness) on SiO<sub>2</sub> that is partly covered by graphene, before (a) and after (b) annealing at 180 °C for 5 min. The dashed white line marks the edge of graphene. c) Raman spectroscopy of graphene-covered regions before and after thermal annealing. The peak at 3055 cm<sup>-1</sup> (star) originates from the *v*'7A mode of PS. d,e) AFM images and corresponding height linescans of PS thin films with (d) and without (e) graphene coverage (linescans taken along white dashed lines). f) AFM images of a PS thin film deposited on top of graphene, before and after the same thermal annealing conditions.

the left half of the film. The monolayer graphene was confirmed via Raman spectroscopy (Figure 1c; Figure S3, Supporting Information) and can be distinguished by a slight color change (due to its 2.3% absorption of white light<sup>[26]</sup>). Upon annealing the sample for 300 s at 180 °C, well above the glass-transition temperature  $(T_{o})$  of PS, the non-graphene-covered regions of the PS film (Figure 1b; right of dash line) were fully ruptured into droplets having micrometer size and a typical height of  $\approx$ 50 nm. In contrast, no dewetting was observed in the regions covered by graphene (Figure 1b, left side). The graphene-capped PS film remains smooth postannealing, with an root mean square (RMS) roughness of 2.1 nm (see atomic force microscopy (AFM) linescan in Figure 1d). The Raman spectrum peak at 3057 cm<sup>-1</sup> for both noncovered and graphene-covered regions (Figure 1c) is characteristic of the v'7A mode of PS<sup>[27]</sup> (benzene ring C-H stretch), verifying that PS remained underneath the graphene after annealing. Control experiments were carried out where PS films were spin-coated on top of graphene to confirm that suppression of dewetting was not due purely to interfacial interactions between PS and graphene (Figure 1f).

To show that dewetting can be suppressed by other 2D materials with Young's modulus comparable to graphene, the same dewetting experiment was repeated with single-layer  $MoS_2$  on 18 nm thick PS. Single-layer  $MoS_2^{[28,29]}$  was grown via CVD and transferred onto a PS thin film (see the Supporting Information). Figure 2 shows a single layer of  $MoS_2$  on PS before

and after dewetting (dewetting was induced by annealing the sample at 180 °C for 300 s). The PS film covered by the  $MoS_2$  monolayer clearly does not undergo dewetting as compared to the uncovered regions which readily dewet.

Our PS dewetting experiments were performed for various PS thicknesses (5, 18, and 60 nm), molecular weights (1.7 and 4.2 kDal), and annealing times (5 and 20 min). In all cases the areas covered by either graphene or  $MoS_2$  showed no dewetting behavior.

To verify the universality of the graphene-capping approach, similar experiments have also been performed on thin films of a semiconducting thienoazacoronene (EH-TAC).<sup>[30,31]</sup> 20 nm EH-TAC thin film was spin-coated from chloroform solution onto a silicon substrate with native silicon oxide layer. Without surface capping layer, EH-TAC thin films can easily dewet upon heating. After annealing at 180 °C for 300 s under nitrogen atmosphere, dewetting can be observed in the EH-TAC thin film under optical microscopy (Figure S2, Supporting Information). However, the EH-TAC film capped by graphene maintains the same surface feature after annealing.

Similar experiments were also performed using metallic thin films. A 20 nm thick polycrystalline gold film was evaporated onto an  $SiO_2$  substrate and covered by graphene. The monolayer graphene layer was clearly discernible in optical microscopy images (**Figure 3**). After annealing at 350 °C for 4 h, significant dewetting occurred in noncovered regions of the





**Figure 2.** Dewetting suppression of a PS thin film by an  $MoS_2$  capping layer. AFM height images and corresponding linescans of  $MoS_2/PS$  a) before and b) after annealing at 180 °C for 300 s (linescans taken along white dashed lines).



**Figure 3.** Dewetting suppression of thin gold films by graphene capping layer. a,b) Optical microscopy images of an Au thin film (20 nm in thickness) on SiO<sub>2</sub> that is partly covered by graphene (the graphene-capped region lies to the left of the vertical dashed line) before (a) and after (b) thermal annealing at 350 °C for 4 h. c) Raman spectra acquired at spots 1–3 in (b). d,e) AFM height images and corresponding linescans of the thermally annealed thin films with (d) and without (e) graphene coverage (linescans taken along white dashed lines).

gold film (Figure 3b, right half of image). AFM imaging showed that, as opposed to the droplets observed in the dewetted PS films, faceted holes and islands formed with angles consistent with Au(111) (Figure 3e). These results indicate that the rupturing of the Au film was due to grain growth and hole formation mechanisms typically encountered during the solid-state dewetting of thin polycrystalline films.<sup>[3]</sup> Again, no detectable dewetting occurred for the graphene-covered regions of the film over large areas, as confirmed in the optical (Figure 3b; left half of sample) and AFM (Figure 3d) images. Thus, the graphene-capping approach is effective in eliminate dewetting for thin films of both polymeric and metallic materials.

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Film dewetting can proceed via either spinodal or nucleation and growth mechanism.<sup>[32-36]</sup> For each process, the onset of dewetting process involves changes in film topography. We hypothesize that if the capping layer can mechanically suppress the film thickness and topography changes, the dewetting process can be controlled. Using the polycrystalline gold film as example, we calculated how an adhered thin layer alters the balance between the surface energies and capping layer deformation. The polycrystalline grains are modeled as close-packed hexagonal cylinders (schematically shown in **Figure 4**a)<sup>[3,32,37]</sup> with width L = 10 h, with h being the thickness of the film and the metal–substrate contact angle  $\theta$  is 60° at equilibrium. The total surface energy E of each grain during the dewetting process can be calculated as a function of the dihedral angle  $\varphi$  between neighboring grains (Figure 4a).<sup>[37]</sup> Here  $\varphi$  is 180° for the initial flat film, and gradually decreases as the grains spheroidize (Figure 4a). Without a capping layer, the lowest *E* for this system is achieved at  $\varphi \sim \theta$ (Figure 4b), where the film breaks into droplets (Figure 4a).

When graphene adheres conformally to the starting thin film, changes in the film surface topology strain the graphene. This leads to an additional term in the deformation energy (graphene is modeled as a stretchable film with thickness 0.34 nm). As shown in Figure 4b, no noticeable change is found in the surface energy  $E-\varphi$  relationship when the Young's modulus of the capping layer is low (Y = 0.01 GPa, or comparable to rubber). The energy landscape noticeably shifts toward higher  $\varphi$  for Y = 4 GPa (comparable to common plastics). However, the new energy minimum at  $\varphi \approx 75^{\circ}$  still corresponds to a regime susceptible to film rupture. For Y = 1 TPa,







**Figure 4.** Energetics analysis of elastic capping layer effect on the dewetting of metallic films. a) Schematic representation of the polycrystalline thin film spheroidization model relating surface free energy to grain size (*L*), film thickness (*h*), dihedral angle between neighboring grains ( $\varphi$ ), and film/ substrate wetting angle ( $\theta$ ). b) Calculated surface free energy change (*E*/*E*<sub>0</sub>) as a function of  $\varphi$  for different Young's modulus of the capping layer (Y). c) Calculated modifications to the spheroidization model assuming different amounts of preexisting compressive strain in the graphene capping layer. d) Generalization of the model demonstrates that the graphene capping layer significantly expands the (I) completely connected region relative to the (II) partially connected region and the (III) dewetted region for different grain configurations in the *L*/*h*- $\theta$  phase diagram.

which corresponds to the actual value for graphene,<sup>[38]</sup> the deformation energy is extremely high, and *E* increases drastically for  $\varphi < 165^{\circ}$  (Figure 4b). This result indicates that the spheroidization/dewetting process is effectively suppressed so that only minimal structural changes ( $\approx 15^{\circ}$  in  $\varphi$ ) can occur at equilibrium.

If the deposited graphene does not completely follow the topology of the underlying thin film, e.g., due to corrugations in graphene,<sup>[39–41]</sup> then there is a decrease in how effective the graphene-capping approach is to suppress dewetting as shown in Figure 4c. However, with 10% preexisting strain, the presence of graphene still shifts the minimum of *E* to  $\varphi \approx 120^\circ$ , a state in which the film is not yet ruptured. Recent experiments indicate that graphene is capable of conformally coating different substrates with high fidelity.<sup>[42–44]</sup> It was shown that graphene conforms to the SiO<sub>2</sub> substrate down to the smallest features with  $\approx$ 99% fidelity. A  $\approx$ 1% preexisting strain in graphene would only minimally affect its capability for dewetting suppression (Figure 4c), emphasizing the robustness of graphene's anti-dewetting quality.

Figure 4d shows the stability phase diagrams for different grain sizes (i.e., L/h ratios) and material–substrate contact angles  $\theta$ . Three stable regions are identified in the diagram, corresponding to (I) completely connected, (II) partially connected, and (III) unconnected grain configurations, respectively.<sup>[35]</sup> The completely connected configuration, i.e., no dewetting, is only achieved for a narrow region where the L/h ratio is small in the absence of a capping layer. A capping layer

with high *Y* significantly expands Region I (red curve), so that a fully connected film is thermodynamically favored over a much wider range of parameters (see the Supporting Information for detailed description of the calculations). At room temperature the metal is immobile and thus kinetically trapped in the form it is deposited. Figure 4 plots the equilibrium energy, meaning that at elevated temperatures, when the metal has enough mobility, it would tend to go to the minimum energy state, which for the case showed in Figure 4b means dewetting (dihedral angle =  $60^{\circ}$ ) at equilibrium. On the other hand, with graphene (Y = 4 GPa) coverage, even at elevated temperatures so that the system again tends to the minimum energy state, the corresponding dihedral angle is still very close to  $180^{\circ}$  and so the film remains connected.

In the case of polymeric thin films, we hypothesize that dewetting suppression also results from damping of surface fluctuations. To demonstrate this, a graphene sheet containing holes of different sizes was deposited onto a PS film (**Figure 5**). Here, the PS film dewets the silicon oxide surface via a spinodal decomposition process and the fluctuation wavelength is measured to be  $\approx 2 \,\mu m$  (Figure S5, Supporting Information). Inside graphene holes with diameters  $\gg 2 \,\mu m$  the PS film was seen to dewet upon annealing into  $\approx 2 \,\mu m$  size features (Figure 5a), in agreement with the estimated spinodal wavelength of this thin film. A decreasing number of peaks and valleys was observed with shrinking hole size. A single dewetted droplet was





**Figure 5.** Lateral confinement effects on spinodal dewetting of a PS film. AFM height scans and corresponding linescans of graphene-capped PS thin films after thermal annealing. Here the graphene capping layer contains holes 7.5  $\mu$ m (a), 1.8  $\mu$ m (b), and 0.5  $\mu$ m (c) in diameter. The vertical red dashed lines in the linescans denote the edges of the holes in the graphene capping layer (linescans taken along white dashed lines).

observed for a hole  $\approx 2 \ \mu m$  in diameter (Figure 5b), while no dewetting were observed for holes smaller than 2  $\mu m$  in diameter (Figure 5c). Thus, the graphene-capping approach can effectively suppress thin film dewetting through the damping of surface capillary waves, due to the extremely high stiffness of the graphene capping layer.

In summary, we have shown that a monolayer 2D capping layer can effectively suppress the dewetting of thin films of polymer, organic semiconductor small molecules, and polycrystalline metal. Thermodynamic modeling indicates that the exceptionally high Young's modulus and surface conformity of 2D capping layers such as graphene and  $MoS_2$  substantially suppress surface fluctuations and thus dewetting. As long as the uncovered area is smaller than the fluctuation wavelength of the thin film in a dewetting process via spinodal decomposition, the dewetting should be suppressed. Our 2D monolayer-capping approach opens up exciting new possibilities to enhance the thermal stability<sup>[45]</sup> and expands the processing parameters for thin film materials without significantly altering their physical properties.

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## **Conflict of Interest**

The authors declare no conflict of interest.

### **Keywords**

anti-dewetting, graphene, metallic thin films, polymeric thin films

# Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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