Supporting Information for

Fabrication and Characterization of Cross-Linked Organic Thin Films with Nonlinear Mass Densities

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I. Infrared (IR) spectroscopy study

Infrared spectra (Figure 4 and Figure S1) exhibited several characteristic peaks; those are attributed due to the different vibrational modes in urea bond. Peaks around 1650 – 1690 cm^{-1} can be assigned to the amide I band with the ν(C=O) stretching vibration mode of the urea group. The band at 1510 cm^{-1} can be assigned to the amide II band with (N–H) bending vibration. Coleman and co-workers has been classified "ordered hydrogen bonded", "disordered hydrogen bonded" and "non-hydrogen bonded" urea, based on amide I characteristic infrared band for urea linkage. These bands were observed at 1630, 1650 and 1690 cm^{-1} respectively.[S1] Therefore from amide I band in IR spectra, we consider that our fabricated polyurea networks were dominated with disordered hydrogen bonded fashion. No peak appeared at 2270 cm^{-1}, indicates no unreacted isocyanate groups are present in polyurea thin films.[S2] The probable reason is that the unreacted isocyanate groups are easily converted to amine by expose to humid air.[S3]

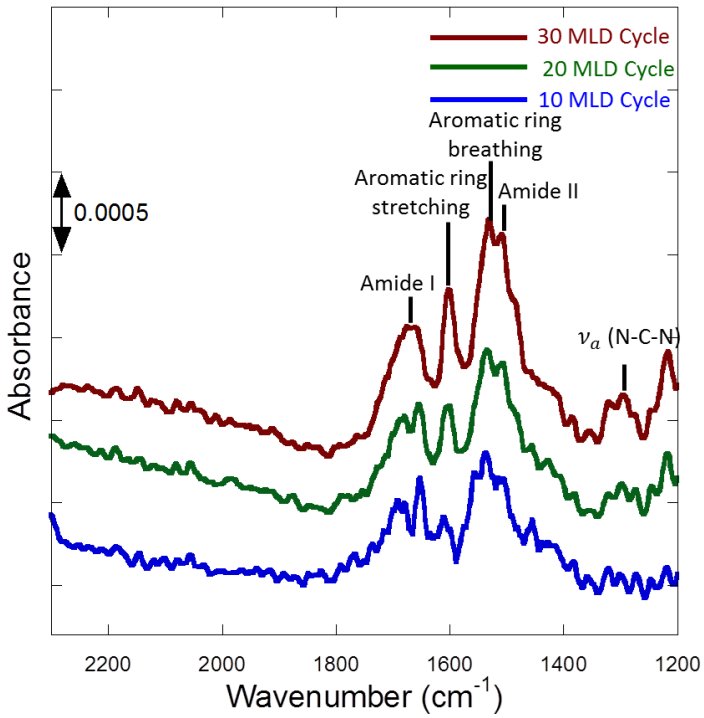


Figure S1. IR spectra of 10, 20, and 30 MLD cycle thin films. Spectra were measured in the region 1200−2300 cm^{-1} under nitrogen atmosphere.

Furthermore, in higher wavenumber region a broad ν(N−H) stretching band appeared at 3255 cm^{-1} (Figure S2), which is the evidence in the presence of wide distribution of hydrogen bonds (with different distances and geometries) that would be expected as disordered hydrogen bonded polyurea networks.[S4,S5]

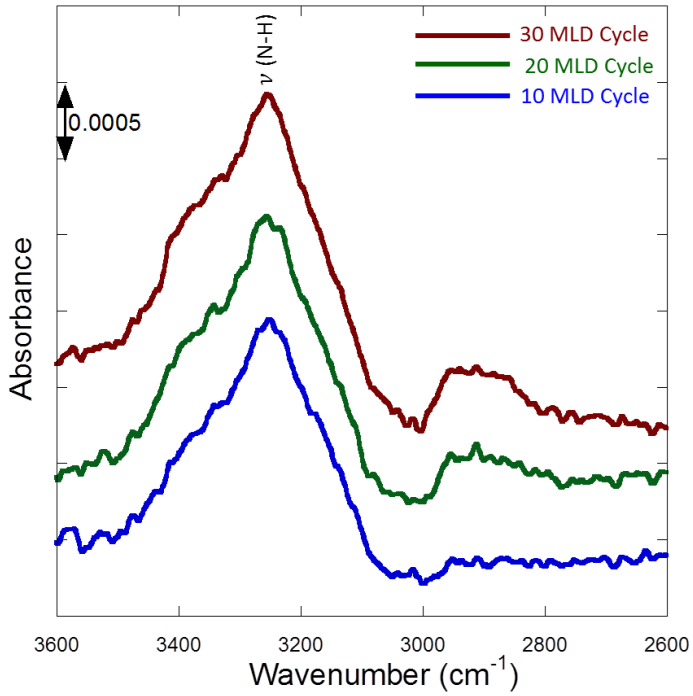


Figure S2. IR spectra of 10, 20, and 30 MLD cycle thin films. Spectra were measured in the region 2600−3600 cm^{-1} under nitrogen atmosphere.

II. X-ray photoelectron spectroscopy (XPS)

Survey scan XPS spectrum of 10, 20, and 30 MLD cycle films were displayed in Figure S3. In addition, survey scan XPS spectrum of APTMS− functionalized surface and bare Si−wafer also provided for comparison. It was revealed that peak intensity of nitrogen and carbon significantly increased with MLD cycles. This result supports the successful multilayer deposition with MLD cycles.

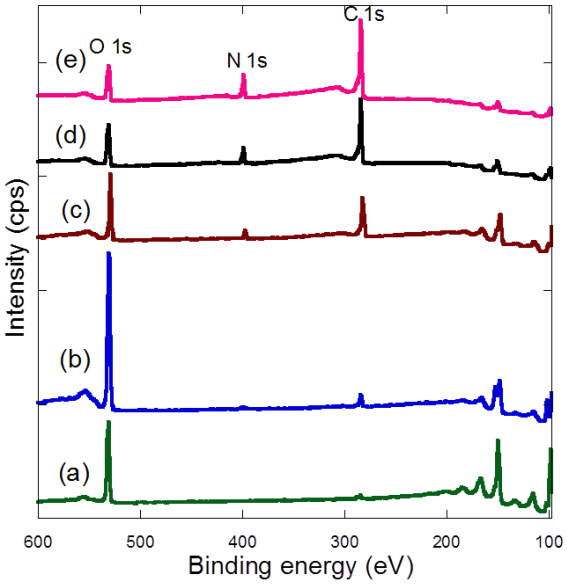
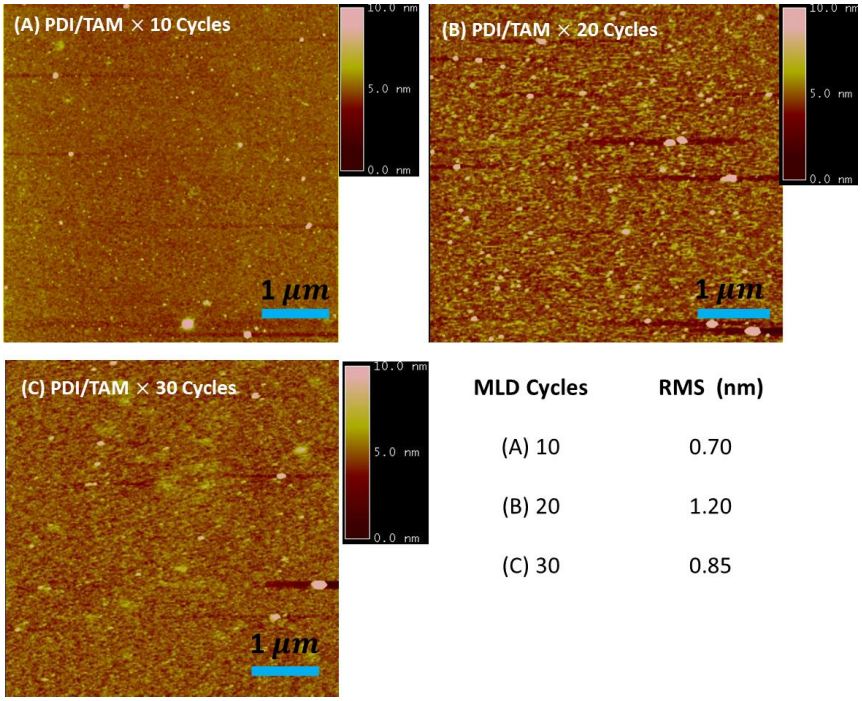


Figure S3. Survey scan XPS spectra (a) Si−wafer (b) APTMS− modified Si wafer (c) 10 MLD cycle (d) 20 MLD cycle (e) 30 MLD cycle thin films.

III. Atomic force microscopy (AFM) for surface morphology

Molecular layer deposition (MLD) technique has an advantage to fabricate smooth films with minimal roughness.[S6] Tapping mode atomic force microscopy (AFM) was carried out to investigate the surface morphology of the polyurea thin films in open atmosphere. Figure S4 represents AFM (height) image of 10, 20, and 30 MLD cycle films. Root mean square (RMS) roughness analysis revealed that a smooth film surface with a maximum roughness is 1.20 nm. Narrow scan area analysis of 10 MLD cycle film show a grain like morphology (Figure S5).



MLD Cycles	RMS (nm)
(A) 10	0.70
(B) 20	1.20
(C) 30	0.85

Figure S4. AFM (height) image for surface morphology (A) 10 MLD cycle, (B) 20 MLD cycle, and (C) 30 MLD cycle films (scan area 5 × 5 μm^2).

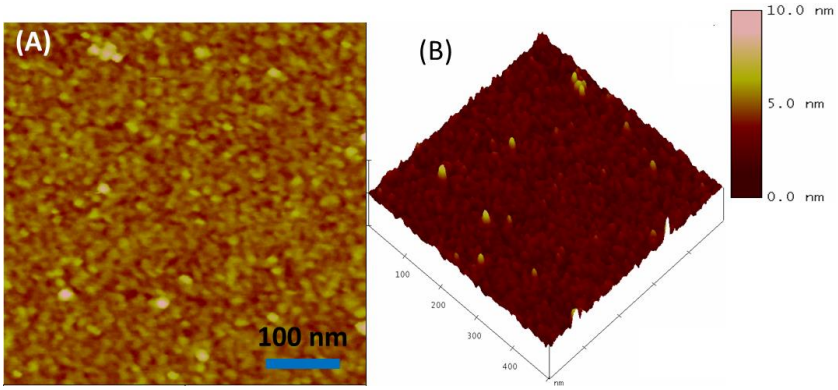


Figure S5. AFM image of 10 MLD cycle film (A) 2D, (B) 3D (scan area 0.5 × 0.5 μm^2).

IV. X-ray reflectivity (XRR) studies on 10, 20, and 30 MLD cycle thin films

For XRR fitting curves, the simulated fringe satisfactorily fit with the experimental fringe profile in the case of 10 MLD cycles with a uniform density. In the case of 20 and 30 MLD cycle films, the results of satisfactory fit with a uniform density could not be obtained. More close fit has been tried with a bilayer model as shown in Figure S6. The fit results were found to improve at the sufficiently satisfactory level. Figure S7 represent the comparison of single layer and bilayer fitting in 30 MLD cycle film.

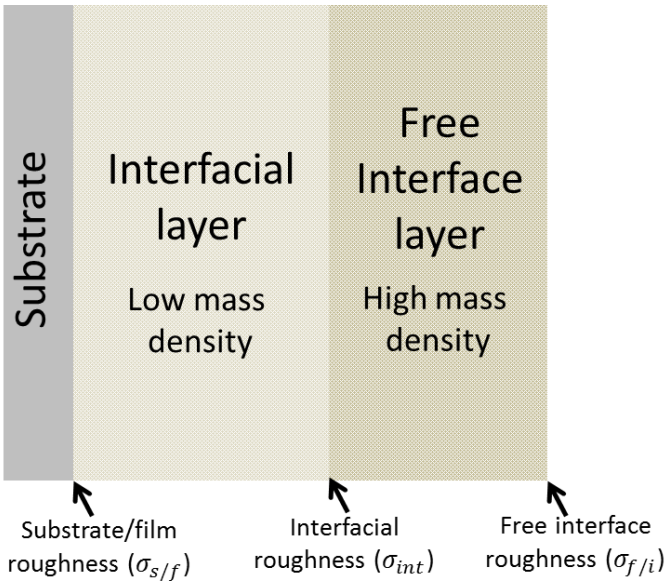


Figure S6. Schematic illustration of layer growth with nonlinear densities.

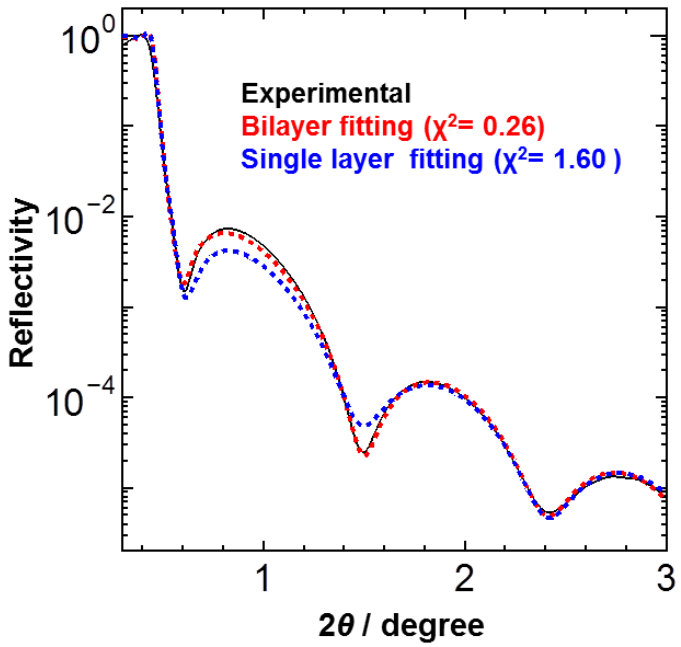


Figure S7. XRR fitting profile of 30 MLD cycle film. Solid line represents experimental data and red dot and blue dot represent bilayer and single layer fitting, respectively.

From XRR density profiles, we estimated mass density (g/cm^3) at 20 and 30 MLD cycle films in free interface (f/i) region and it was higher than mass density of interfacial layer (int.) region (Figure 7).

Followed by roughness, 20 and 30 MLD cycle films was demonstrated three different roughness parameters; roughness between substrate and thin film ($\sigma_{s/f}$), roughness in free interface ($\sigma_{f/i}$) and interfacial roughness of different densities adjacent layers (σ_{int}) (Figure S6). In this present work, the roughness between substrate and thin film ($\sigma_{s/f}$) was considered as constant, $\sigma_{s/f} = \sigma_{Si} = 0.5$ nm, which was determined by XRR measurement of a blank silicon wafer.

The interfacial roughness (σ_{int}) of thin films is larger than free interface roughness ($\sigma_{f/i}$) (Table S1). This may happen due to the close contact between different densities neighboring layers. Thus, it is reasonable to infer that different mass densities are arisen into thin films. And, this may happen because of different conformational arrangement of molecular networks in different distance from the substrate surface. We presumed that, this interfacial transformation occurred because of different degree of cross-linked among layers proximate to the substrate surface and those of extending away from the surface.

Table S1: Thickness, *d*, mass density, ρ, and roughness, σ of reported layers of 10, 20, and 30 MLD cycle thin films were extracted from XRR profile shown in Figure 6. The statistical errors are shown in each value.

No. of MLD cycles	Layer name	Thickness, *d* (nm)	Mass density, ρ (g/cm^3)	Roughness, σ (nm)
10	Si wafer	0.00	2.33	0.5 ($\sigma_{s/f}$)
	Film	4.55 $\pm$ 0.03	1.33 $\pm$ 0.01	0.57 $\pm$ 0.03 ($\sigma_{f/i}$)
20	Si wafer	0.00	2.33	0.5 ($\sigma_{s/f}$)
	Film	4.89 $\pm$ 0.06 (int.)	1.40 $\pm$ 0.02 (int.)	0.85$\pm$ 0.3 (σ_{int})
		1.70 $\pm$ 0.06 (f/i)	1.61 $\pm$ 0.05 (f/i)	0.74 $\pm$ 0.04 ($\sigma_{f/i}$)
30	Si wafer	0.00	2.33	0.5 ($\sigma_{s/f}$)
	Film	3.73 $\pm$ 0.14 (int.)	1.43 $\pm$ 0.03 (int.)	0.68 $\pm$ 0.27 (σ_{int})
		5.71 $\pm$ 0.15 (f/i)	1.67 $\pm$ 0.04 (f/i)	0.60 $\pm$ 0.07 ($\sigma_{f/i}$)

$\boldsymbol{\sigma}_{s/f}$ denotes roughness of substrate/film interface, $\boldsymbol{\sigma}_{f/i}$ denotes roughness of free interface and $\boldsymbol{\sigma}_{int}$ represent interfacial roughness of different densities layers into thin films.

V. Grazing incidence small angle X-ray scattering (GI-SAXS) studies on 10 MLD cycle film

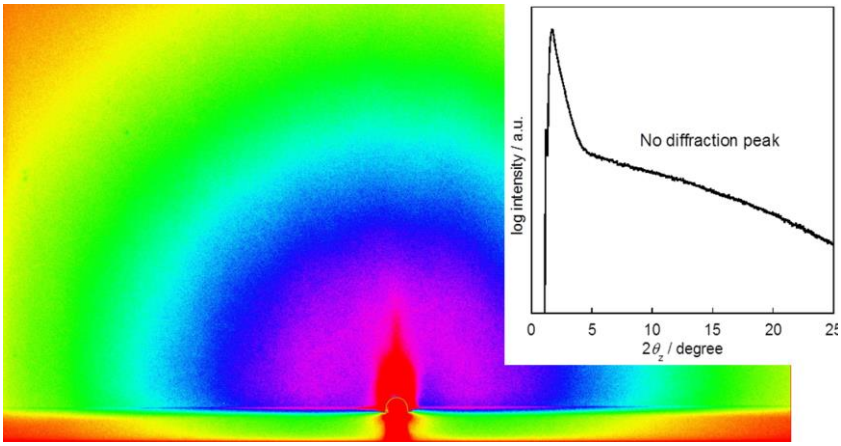


Figure S8. 2D GI-SAXS imaging plate pattern of the 10 MLD cycle film on a Si wafer.

1D profile in the out-of-plane direction extracted from the 2D GI-SAXS pattern.

Supplementary references

(S1) Coleman, M. M.; Sobkowiak, M.; Pehlert, G. J.; Painter, P. C.; Iqbal, T. Infrared Temperature Studies of a Simple Polyurea. *Macromol. Chem. Phys.* **1997**, *198*, 117-136.

(S2) Kim, A.; Filler, M. A.; Kim, S.; Bent, S. F. Layer-by-Layer Growth on Ge (100) via Spontaneous Urea Coupling Reactions. *J. Am. Chem. Soc.* **2005**, *127*, 6123-6132.

(S3) Kim, M.; Byeon, M.; Bae, J-S.; Moon, S. Y.; Yu, G.; Shin. K.; Basarir, F.; Yoon, T. H.; Park, J-W. Preparation of Ultrathin Films of Molecular Networks through Layer-by-Layer Cross-Linking Polymerization of Tetrafunctional Monomers. *Macromolecules* **2011**, *44*, 7092-7095.

(S4) Coleman, M. M.; Skrovanek, D. J.; Howe, S. E.; Painter, P. C. On the Validity of a Commonly Employed Infrared Procedure used to Determine Thermodynamic Parameters Associated with Hydrogen Bonding in Polymers. *Macromolecules* **1985,** *18*, 299-301.

(S5) Coleman, M. M.; Lee, K. H.; Skrovanek, D. J.; Painter, P. C. Hydrogen Bonding in Polymers. 4. Infrared Temperature Studies of a Simple Polyurethane. *Macromolecules* **1986,** *19*, 2149-2157.

(S6) Johnson, P. M.; Yoon, J.; Kelly, J. Y.; Howarter, J. A.; Stafford, M. Molecular

Layer-by-Layer Deposition of Highly Crosslinked Polyamide Films. *J. Polym. Sci. Part B: Polym. Phys.* **2012,** *50*, 168-173.