

Supplementary Material for

Aluminum Oxide Free-Standing Thin Films to Enable Nitrogen Edge Soft X-ray Scattering

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1. Materials and methods

Al₂O₃ window fabrication

Double-sided polished 4-inch p-type <100> silicon wafers, 525 μm in thickness with ± 1 μm thickness variation from the center, were purchased from Virginia Semiconductor. A 46 nm thick Al₂O₃ film was grown on the surface of the silicon wafer using a Cambridge Savannah 200 Atomic Layer Deposition (ALD) tool in the Nanofabrication Laboratory at the Pennsylvania State University. Trimethylaluminum (TMA; Al(CH₃)₃) and water (H₂O) were used as precursors for deposition. The temperature was held at 250 °C for 435 cycles. The Al₂O₃-coated wafers were then patterned by photolithography. Al₂O₃-coated wafers were baked on a hot plate for 3 minutes at 100 °C to remove water. Then, the side without Al₂O₃ was spin coated with hexamethyldisilazane (HMDS) to promote adhesion of photoresist to the wafer. Next, three layers of the polymer photoresist SPR 955 were spin coated on top of the HDMS to give a total photoresist thickness of 8 μm . Lithography features were transferred to the resist-coated wafer using a

chromium mask under ultraviolet light in a Karl Suss MA/BA6 with contact for 3 cycles of 12 seconds each. The resist was then developed using MFCD26 for 90 seconds. After resist development, the wafer was transferred to an Alcatel Speeder 100 Si DRIE system for etching. Sulfur hexafluoride (SF₆) and octafluorocyclobutane (C₄F₈) were used as etching gases and the etch rate was 7-10 μm/min. It takes around 55 minutes to etch 525 μm silicon. After etching, the photoresist was removed from the etched wafer by dissolving it in PRS3000 at 85 °C for 15 minutes. The wafer was then rinsed with acetone, isopropanol, and ultrapure water three times each. Afterwards, individual Al₂O₃ windows were obtained by cleaving the etched wafer into small pieces using a silicon scriber.

Spectroscopic ellipsometry

The thickness of Al₂O₃ windows was determined using a J.A. Woollam RC2 ellipsometer. Ellipsometry measurements were performed at 55°, 65°, and 75°. The silicon substrate was modeled as silicon with a 2 nm layer of native oxide. The film thickness of the Al₂O₃ layer was determined using the Cody-Lorentz model.

Polymer films preparation

Poly(3-hexylthiophene-2,5-diyl) (P3HT) was purchased from Merck and poly((9,9-bis-(2-octyl)flourene-2,7-diyl)-*alt*-(4,7-di(thiophene-2-yl)-2,1,3-benzothiadiazole)-5',5''-diyl) (PFTBT) was purchased from Lumtec with PFODBT as the product name. The block copolymer poly(3-hexylthiophene-2,5-diyl)-*block*-poly((9,9-bis-(2-octyl)flourene-2,7-diyl)-*alt*-(4,7-di(thiophene-2-yl)-2,1,3-benzothiadiazole)-5',5''-diyl) (P3HT-*b*-PFTBT) was synthesized using previously published methods¹. 10 mg/mL P3HT, 10 mg/mL PFTBT, and 5 mg/mL P3HT-*b*-PFTBT were dissolved in chloroform (Sigma) at 80 °C overnight inside a glove box. Then, the solutions were passed through 0.2 μm PVDF filters (Whatman). The filtered solutions were spin casted on a

silicon wafer at 800 rpm for 1 min. For NEXAFS experiments, the polymer solutions were directly spin cast on a silicon substrate. For RSoXS experiments, silicon substrates were first spin coated with poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) solution (Clevios P, Heraeus) that was filtered using a 0.45 μm PVDF filter (Whatman). Then, the as-cast films were floated by immersing the substrates into DI water. The floated films were picked up on 50 nm thick Si_3N_4 windows with a 5 mm $\times$ 5 mm frame size (Norcada) or on 46 nm thick Al_2O_3 windows fabricated in-house. The RSoXS samples and NEXAFS samples were further annealed at 165 $^\circ\text{C}$ for 1 hour inside a nitrogen glovebox on a temperature controlled hotplate.

Near edge X-ray fine structure (NEXAFS) spectroscopy

Total electron yield (TEY) NEXAFS spectra of polymer films were collected at beamline 11.0.1.2 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory². The silicon substrates were mounted on the sample bar using doubled-side carbon conducting tape. The angle between the incident X-ray beam and the substrate was kept at 55 $^\circ$. The collected TEY spectra were first normalized by the direct beam flux. Then the background from the silicon substrate was subtracted by fitting the pre-edge data with a linear function.

Resonant soft X-ray scattering

RSoXS experiments were carried out at beamline 11.0.1.2 at the ALS in transmission geometry using a charged coupled detector.² A q range of 0.0013 $\text{\AA}^{-1}$ to 0.08 $\text{\AA}^{-1}$ was obtained by using two different sample to detector distances (50 mm and 150 mm). 2D images were corrected for solid angle geometry, dark counts, exposure time, and incident beam flux variation using the Nika software package.³ A direct beam flux scan was recorded using a photodiode detector to account for flux variations with energy. The scattering profiles were obtained by azimuthally integrating the 2D images. Scattering data from bare Si_3N_4 and Al_2O_3 windows were also collected.

Atomic force microscopy

Atomic force microscopy (AFM) images were taken with a Bruker Dimension Icon ScanAsyst operating in PeakForce Tapping mode. A ScanAsyst Air (Bruker) tip was used. 1 μm x 1 μm scans were acquired using a scan rate of 1.0 Hz at a peak force set point of 8 to 12 nN (512 samples/line). Micrographs were first-order flattened to remove scan defects using NanoScope Analysis.

2. AFM images of Al_2O_3 and Si_3N_4 windows

Figure S1 shows AFM images of both Al_2O_3 and Si_3N_4 films used as RSoXS windows. The root mean square of the variation in topology is taken to be the surface roughness, which is 0.41 nm for Al_2O_3 and 0.42 nm for Si_3N_4 .

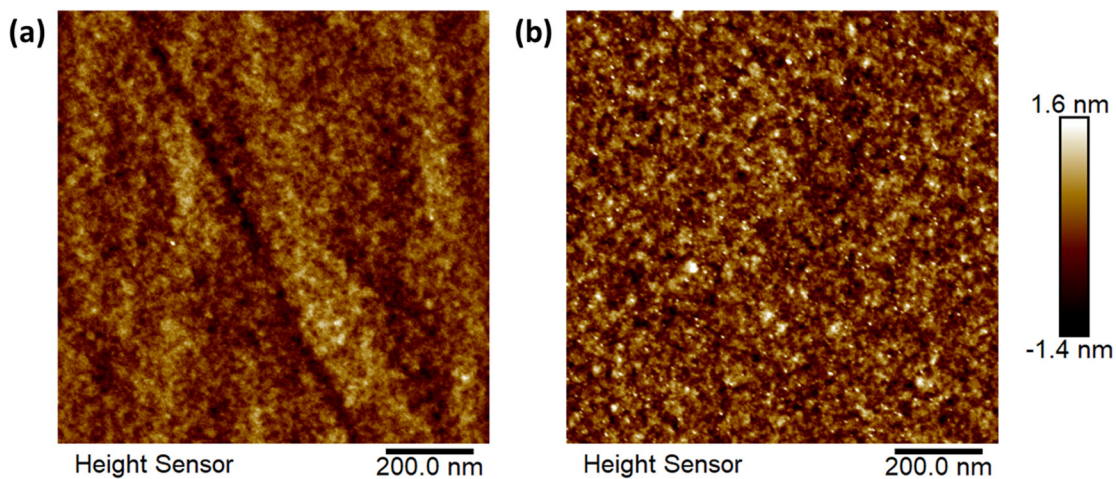


Figure S1. AFM images of (a) 46 nm thick Al_2O_3 and (b) 50 nm thick Si_3N_4 films used as RSoXS windows.

3. RSoXS data from Al₂O₃ and Si₃N₄ windows at 398.2 eV (onset of nitrogen K-edge)

In addition to the data shown in Figure 2 of the main text at 285 eV and 410 eV, we show data from bare Al₂O₃ and Si₃N₄ windows at the onset of the nitrogen edge, 398.2 eV, in Figure S2.

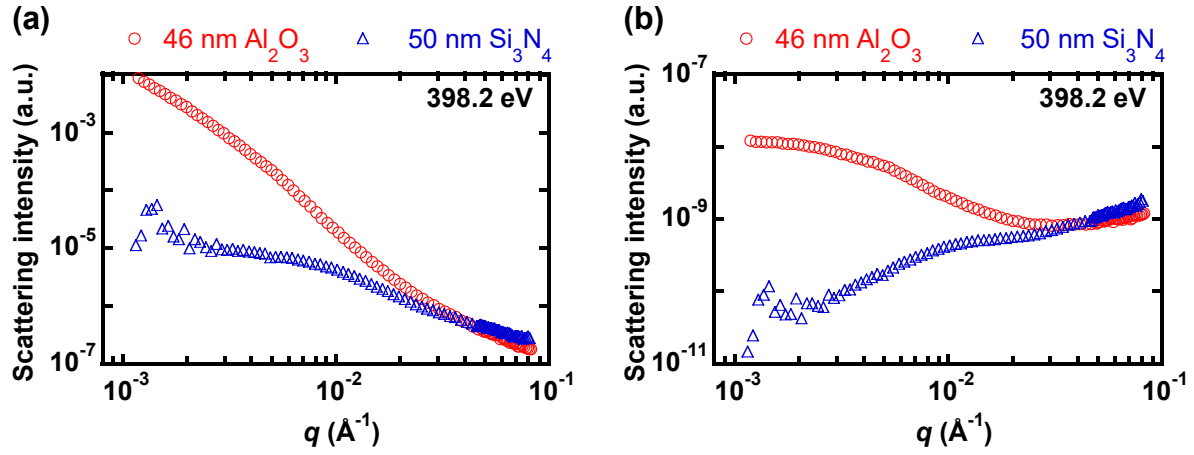


Figure S2. (a) RSoXS profiles at 398.2 eV (onset of nitrogen K-edge) for Al₂O₃ and Si₃N₄ windows. (b) Same data as (a), but plotted as Iq^2 versus q .

4. Scattering contrast of Al₂O₃ and Si₃N₄ with respect to vacuum

The scattering contrast of Al₂O₃ ($\rho = 3.95 \text{ g/cm}^3$) and Si₃N₄ ($\rho = 3.17 \text{ g/cm}^3$) with respect to vacuum was calculated using the theoretical real (δ) and imaginary (β) components of the refractive index (n):

$$n(\lambda) = 1 - \delta(\lambda) + i\beta(\lambda)$$

from the Henke database⁴ where λ is the wavelength of the incident X-rays. The scattering contrast

($\frac{\Delta n \Delta n^*}{\lambda^4}$) of the windows with respect to vacuum is calculated by:

$$\frac{\Delta n(\lambda) \Delta n^*(\lambda)}{\lambda^4} = \frac{\delta(\lambda)^2 + \beta(\lambda)^2}{\lambda^4}.$$

As shown in Figure S3, the scattering contrast between Al₂O₃ and vacuum is higher than the scattering contrast between Si₃N₄ and vacuum.

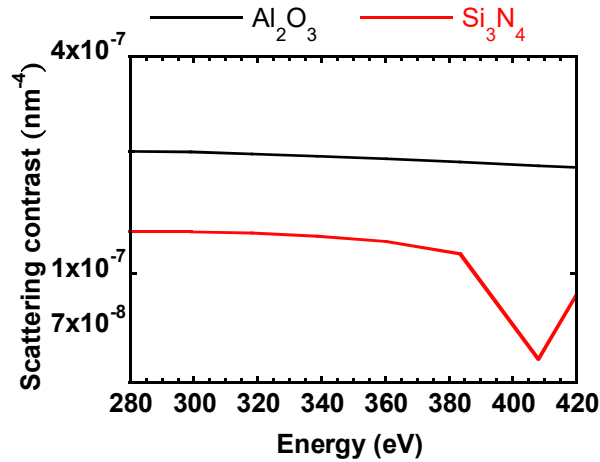


Figure S3. Scattering contrast of Al₂O₃ and Si₃N₄ with respect to vacuum.

5. The influence of fluorescence background on Kratky plots

The effect of fluorescence background on scattering profiles was modeled using a broad peak function from NCNR Macro⁵ with

$$I(q) = \frac{10^{-5}}{q^3} + \frac{10}{1 + 50(q - 0.02)^2} + 0.01 + FL$$

where q is the scattering vector and FL represents the fluorescence background. As shown in Figure S4, as the fluorescence background increases, the tail of the scattering profile in a Kratky plot goes up, and it can mask structural features in the sample.

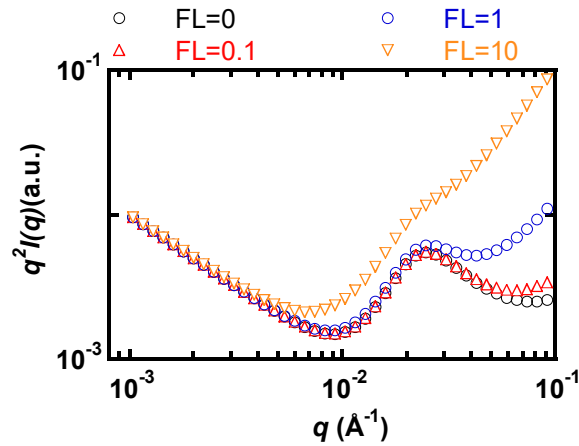


Figure S4. Kratky plots of a broad peak function with a structural feature near $q = 0.02 \text{ \AA}^{-1}$ with different levels of fluorescence background.

6. Kratky plots of scattering from Al₂O₃ and Si₃N₄ windows

The shapes of Kratky plots of a 46 nm thick Al₂O₃ substrate near the C K-edge (285 eV) and the N K-edge (398.2 eV and 410 eV) are very similar as shown in Figure S5a. The differences could arise from RSoXS at 285 eV being sensitive to potential carbon contamination on the Al₂O₃ substrate or on the optics. In contrast, the shape of Kratky plots for a 50 nm thick Si₃N₄ substrate near the C K-edge (285 eV) and the N K-edge (398.2 eV and 410 eV) are different as shown in Figure S5b. At the C K-edge (285 eV), the high q region flattens out above $q = 0.01 \text{ \AA}^{-1}$ while at the N K-edge, there is an upturn above $q = 0.02 \text{ \AA}^{-1}$. This upturn is a signature of fluorescence background.

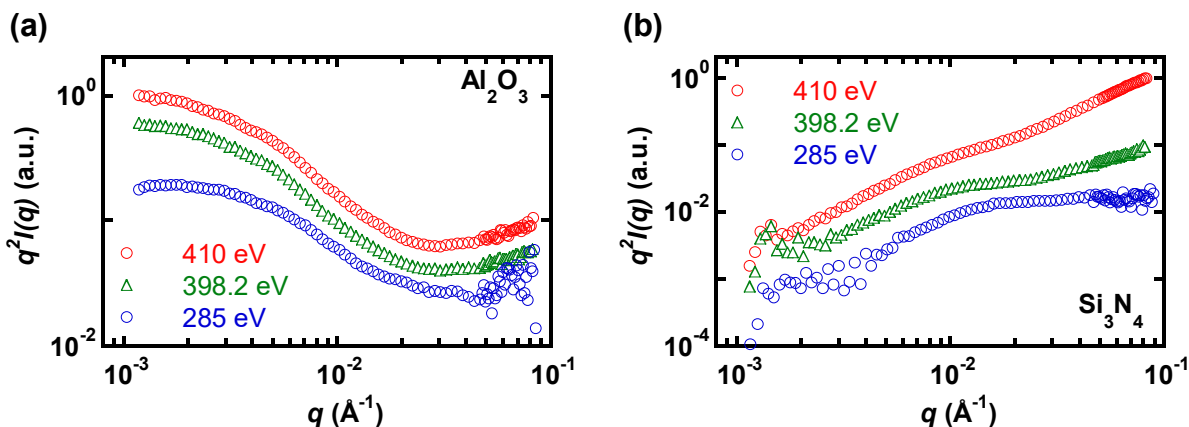


Figure S5. Kratky plots of (a) 46 nm thick Al₂O₃ and (b) 50 nm thick Si₃N₄ substrates at 285 eV (C K-edge), 398.2 eV (onset of N K-edge), and 410 eV (N K-edge). Data are offset for clarity.

7. RSoXS data from block copolymer films at the onset of the nitrogen edge (398.2 eV)

In addition to the RSoXS data shown in Figure 4 of the main text at 285 eV and 410 eV, we show data from P3HT-*b*-PFTBT on Al₂O₃ or Si₃N₄ windows at the onset of the nitrogen edge, 398.2 eV, in Figure S6.

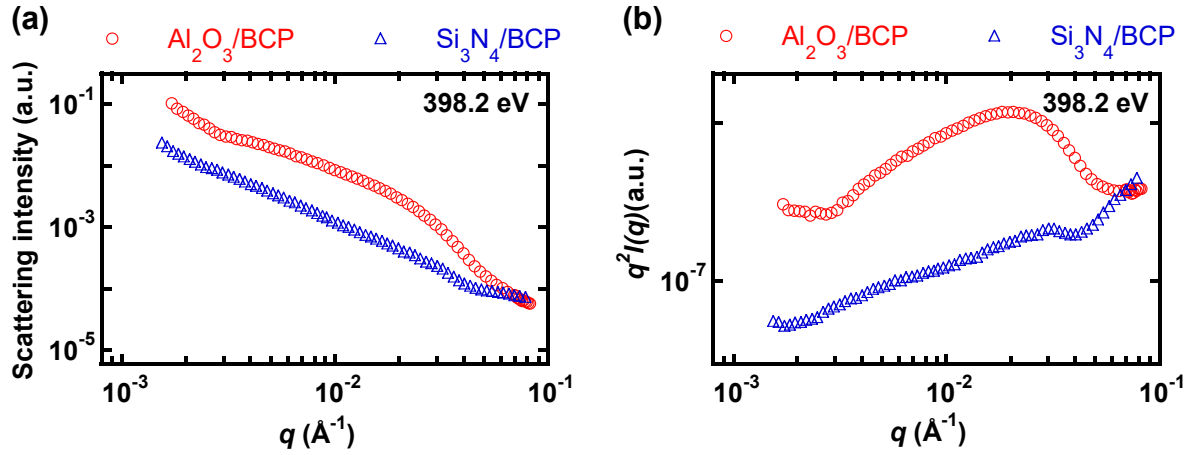


Figure S6. (a) RSoXS profiles of P3HT-*b*-PFTBT (BCP) supported on a 46 nm thick Al₂O₃ substrate or a 50 nm Si₃N₄ thick substrate at the onset of the nitrogen K-edge (398.2 eV). (b) Same data as (a) plotted as Iq^2 vs q

8. References

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