Substrate Effects on Perfluorinated-Sulfonic Acid Polymer Thin Films

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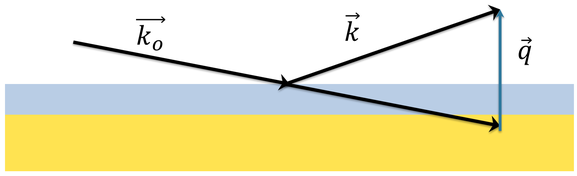
Introduction

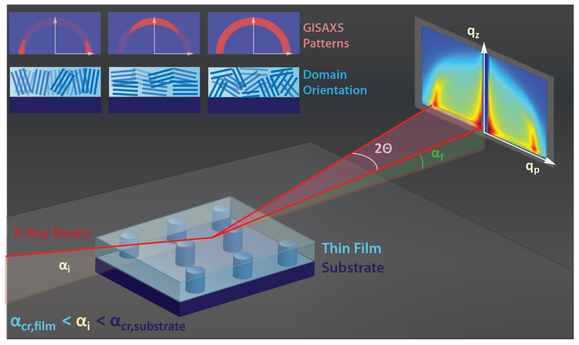
- PFSA ion-conducting polymer (ionomer) is used in Fuel Cells and other Electrochemical Technologies as a membrane separator and catalyst layer component to conduct ionic species to and from the active catalyst nanoparticles
- As ionomer thickness is reduced, substrate interactions increasingly influence ionomer morphology and resulting transport properties
- Elucidating the effect of interfacial interactions on the structure/property relationship is crucial to mitigating current catalyst layer limitations

Methodology

- Grazing Incidence Small Angle X-Ray Scattering is used to probe the morphology of ionomer thin-films
- Incident X-Rays are scattered by electrons
- Variation in the electron density of a sample will cause non-uniform scattering and appears as peaks in the 2D images
- Scattering data can give qualitative and quantitative information of a sample's structure including domain shape and spacing



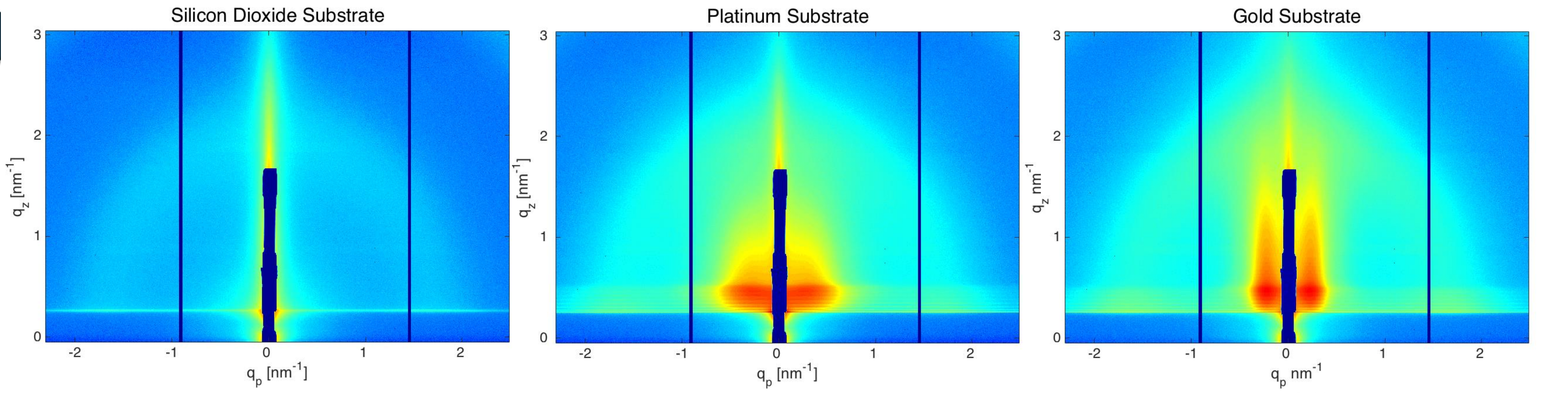
$$\vec{q} = \vec{k} - \vec{k}_o \qquad I(\vec{q}) = \sum_j \sum_k b_j b_k e^{\vec{q}\cdot\vec{r}_{jk}}$$



Results

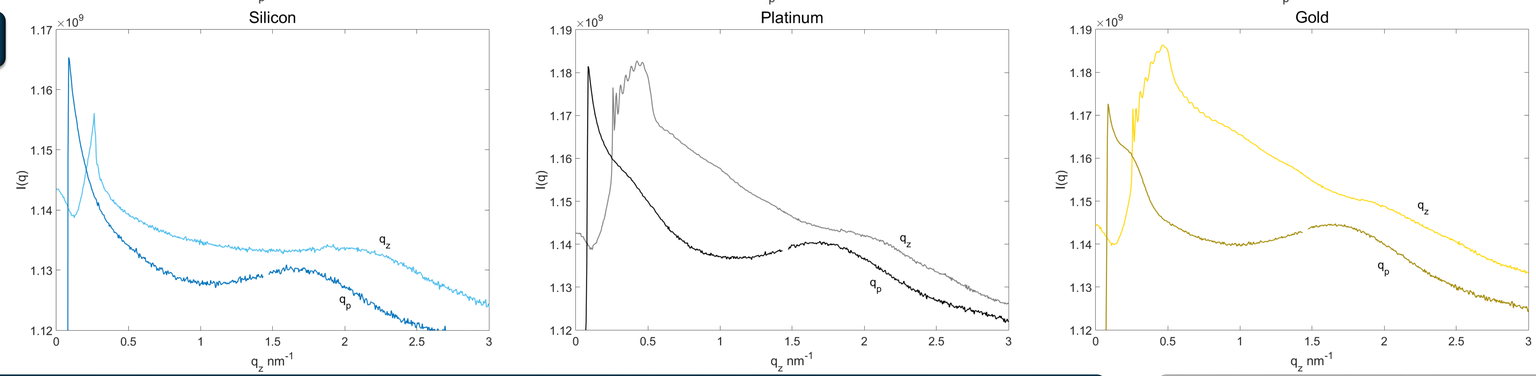
2D GISAXS Profile

- Broad halo is characteristic of phase separated poly-electrolytes and attributed to ionic domain spacing
- The ring is isotropic on SiO_2, anisotropic on Au and Pt, indicating preferential ordering induced from increased substrate interaction



1D Line Profiles

- Profiles are taken in the q_p and q_z directions to examine ordering in- and through- plane, respectively
- Off-Specular Kiessig Fringes are present on Platinum and Gold, which arise from interference of X-Rays, and enhance structural information



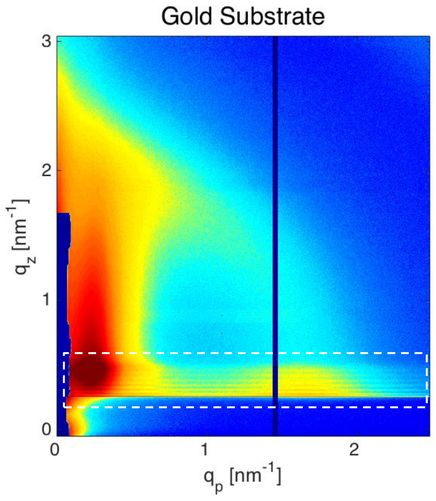
Ionic Domain Confinement

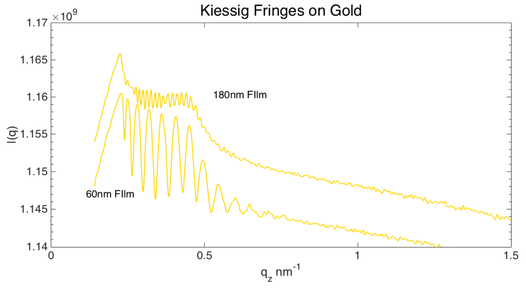
- Ionomer peak appears at larger q for q_z linecuts, indicating reduced ionic domain spacing through-plane
- Reduced spacing through-plane is present regardless of substrate and points to confinement effects in thin films

Substrate Induced Ordering

- Gold and Platinum substrates induce paracrystalline ordering, which is apparent from the bright red flares in the 2D GISAXS images
- Paracrystalline peak appears at lower q on gold, which corresponds to longer range inter-crystalline spacing

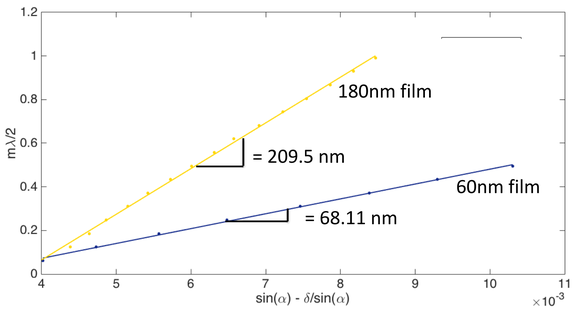
X-Ray Standing Waves and Bragg Analysis





- Reflections at the surface vs. inside the film creates differences in path length and causes X-Ray Standing Waves in the scattering pattern
- The modified Bragg Equation can be used to extract the correlation length and critical angle of the film

$$m\lambda = 2\Lambda\left(\sin[\alpha] - \frac{\delta}{\sin[\alpha]}\right)$$



- Correlation length overestimates film thickness compared to ellipsometry, but has the advantage of being in-situ

Conclusions

- Ionic domains have smaller d-spacing on all substrates due to confinement effects of thin films
- Gold and Platinum induce ordering of the paracrystalline peak, which may impact transport properties and is relevant to ionomer-catalyst interactions in the catalyst layer
- Gold and Platinum also enhance X-ray standing waves, which can be used in-situ to monitor film thickness and may be used to extract additional structural information

Acknowledgements

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