Mid-Infrared Transparent Substrate for Alkylsiloxane Monolayers

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Abstract:
An infrared (IR) and visible transparent substrate compatible with alkylsiloxane monolayers was fabricated by coating a calcium fluoride window with SiO$_2$ by atomic layer deposition (ALD). Octadecylsilane (ODT) monolayers adsorbed to the SiO$_2$-covered CaF$_2$ substrates were found to be equivalent to ODT monolayers on glass in terms of water contact angle and vibrational spectra. The substrate was also used as a platform for thiocyanate, t-butyl ester, and hydroxyl-terminated monolayers.

Summary of Research:
Self-assembled monolayers (SAMs) can be used to create highly ordered surfaces having tunable chemical functionalities. Alkylsiloxane monolayers are simple to apply, stable in a wide range of physical and chemical environments, and do not degrade appreciably even over periods of months [1]. These attributes make them ideal platforms for probing the interaction of water with various surfaces. However, the most important substrates compatible with alkylsiloxane monolayers, the silicon oxides, are not transparent through most of the infrared region. Since water also has strong absorption bands in the IR region, spectroscopy of vibrational transitions at the water-alkylsiloxane SAM interface is greatly complicated in both transmission and reflection geometries.

In this project CaF$_2$ (transparent 0.2-10 μm) was coated with a thin film of SiO$_2$ to create an IR and visible transparent substrate capable of functionalization by alkylsiloxane monolayers. Clean, optically polished CaF$_2$ was coated with 10 nm of SiO$_2$ with the Oxford ALD FlexAL. Deposition of SiO$_2$ on bare CaF$_2$ results in a substrate with SiO$_2$ on both sides. To modify a single side of the CaF$_2$, a protective mask of photoresist was spin-coated onto one face. After ALD of SiO$_2$, the substrate was sonicated in a stripping solution to remove the mask. An octadecylsilane monolayer was then applied to the substrate by adsorption from dilute solution.

The stationary contact angle of water on OTS was found to be the same whether the SAM was deposited on glass or SiO$_2$-coated CaF$_2$. IR spectra of the modified CaF$_2$ show that the thin SiO$_2$ layer did not absorb in the IR significantly above 1250 cm$^{-1}$ (Figure 1). In addition, IR spectra of OTS on the modified CaF$_2$ substrate matched those of OTS on glass.

The SiO$_2$ deposited on the CaF$_2$ was later increased to a nominal thickness of 50 nm for a more robust film. X-ray photoelectron spectroscopy in conjunction with argon ion milling was used to determine the elemental profile of this substrate. It indicated a transition from SiO$_2$ to CaF$_2$ over ~10 nm, and a film thickness of ~39 nm (Figure 2).

The substrate was also used as a platform for thiocyanate, t-butyl ester, and hydroxyl terminated SAMs using silane chemistry. In the future new functionalities and mixed monolayers will be applied.

References:
Figure 1: Absorbance of 1 mm thick bare CaF$_2$ (dashed line), 1 mm thick SiO$_2$ (dotted line) and 10 nm SiO$_2$ on CaF$_2$ (solid line) in the IR region.

Figure 2: Elemental profile of SiO$_2$ film (nominal thickness 50 nm) on a CaF$_2$ substrate as measured by x-ray photoelectron spectroscopy and ion milling.