Substrate-Induced Order in Phosphonate-Metal Ion Multilayers

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Introduction

The coating, functionalizing, or patterning of inert substrates such as Si wafers is an important step in designing two-dimensional electronic or magnetic devices. The incorporation of metal ions into organic networks is particularly important for tailoring specific electronic or magnetic properties.

Little is known, however, on the effect that the substrate may exert on the metal ions, including a possible competition between the interactions of metal ion/organic headgroup and metal ion/substrate.

Methods and Materials

We have prepared self-assembled multilayers of biphosphonic acid Ethyldihydrogenphosphate-perylene(dicarboximide), or EPPI, alternating with Zr^{4+} ions. The organic EPPI molecule is essentially rod-like and is functionalized with phosphonic acid groups at both ends, allowing it to coordinate metal ions and incorporate them into the organic network.[1] In contrast to the standard method of building up multilayers (the Langmuir-Blodgett or LB technique, in which the films are transferred from a monolayer spread on water), here the multilayer is formed by direct absorption from solution – alternating between EPPI and Zr^{4+} ions from an aqueous solution.

These multilayers were investigated by specular x-ray reflectivity (XR), i.e., by recording the reflected intensity as a function of the surface-normal momentum transfer, q_z.

XR yields the surface-normal density profile and is therefore the method of choice if the structure of a thin film on a substrate is of interest.

Results

The Fresnel-normalized reflectivity (i.e., the reflectivity from the film on Si divided by the ideal Fresnel reflectivity from a flat Si substrate), R/R_f of 15 layers of EPPI and Zr is shown in Fig. 1.

It should be noted that the reflectivity shown here spans nine orders of magnitude in intensity (before being normalized). This impressive dynamic range can only be achieved with brilliant synchrotron x-ray sources such as the APS, that provide a large number of incident photons and allow the user to focus those photons on the sample even at grazing angles.

Three features or the absence thereof are clearly discernible in the measured reflectivity. (1) Pronounced oscillations, also known as Kiessig fringes, indicate the overall thickness of the film, which varies from16 to 18 nm, depending on which spot the x-ray beam probes on the sample. (2) There is no indication of multilayer peaks, which would be expected if the Zr layers were well-ordered. Such multilayer peaks are often observed in LB films but are obviously absent in this case, indicating that the Zr ions are dispersed in a disordered way within the organic EPPI matrix. (3) The most interesting and unexpected feature is the broad quasi-Bragg peak centered at around 5.5 nm^{-1} . This peak can be explained by partial ordering or layering of the Zr ions close to the Si substrate. Detailed analysis and fitting of a model density profile to the data shows that only three to four Zr layers are ordered and that the ordering decays rapidly with increasing distance from the Si substrate (decay length: 1.2 nm). The distance between the ordered Zr layers is about 1.2 nm, as expected from the length of the EPPI rods.

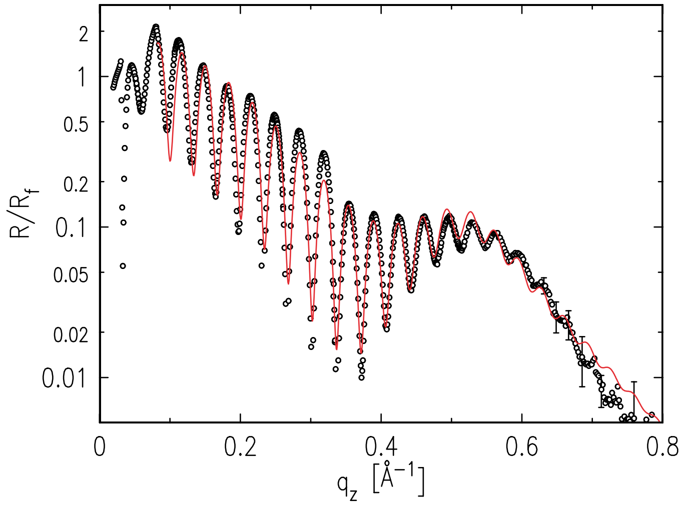

FIG. 1. Fresnel normalized reflectivity from 15 layers of EPPI and Zr as deposited alternatingly on a Si substrate as a function of the surface-normal momentum transfer q_z . The red line represents the best fit of the data to a model of decaying layers of Zr in the vicinity of the Si substrate.

Discussion

To our knowledge, this is the first time that substrate-induced layering has been found for organic films on a substrate. The possibility of substrate-induced ordering is obviously of great importance for the design of two-dimensional networks. Similar ordering phenomena have been found for liquid crystal surfaces, liquid metal surfaces, and liquids in contact with a substrate.

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References

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