Specular X-ray Reflectivity Study of Ordering in Self-Assembled Organic and Organic-Inorganic Electro-Optic Multilayer Films

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Introduction

Siloxane-based layer-by-layer self-assembly (SA) is a challenging yet promising approach to the incorporation of oriented organic molecules or inorganic building blocks into thin films and thereby to the formation of photonically/electronically functional superlattices.[1-4] We have used specular x-ray reflectivity (XRR) to study structural ordering in organic and organic-inorganic SA electro-optic superlattices based on using an all-"wet-chemical" approach to self-assembled superlattice (SAS) refractive index tuning achieved by intercalating layers of gallium or indium oxide while retaining matrix acentricity, large electro-optic responses, and microstructural regularity.[5,6]

Methods and Materials

In the present study, substrate cleaning procedures, chromophore synthesis, schemes for the SA of siloxane-based chromophoric superlattices without and with incorporation of refractive index modifying Ga or In oxide layers, and film analyses were similar to those previously reported.[5,6] XRR studies were performed using a Huber diffractometer in the specular reflection mode.

Results and Discussion

We compare x-ray reflectivity results for multilayers prepared by repeating the three layer-building deposition steps. Samples with up to five chromophore layers were studied. The multilayer reflectivity data were fitted using using a Gaussian-step model.[7] The fitting parameters were (i) the thickness of film, (ii) the film electron density, and (iii) the root-mean-square width of each interface. The film thickness increases linearly with the number of added layers for SA organic films and for SA films with incorporated Ga or In oxide layers (and the additional polysiloxane capping layer of about 8 Å thickness). From the slope of the XRR data, an average interlayer spacing can be deduced: 20.2±0.5 Å (SA organic films), 62±3 Å (SA gallium-containing films) and 70±3 Å (SA indium-containing films). The linearity demonstrates that self-assembled multilayers produced by the present approach possess high structural regularity. Even though the absolute value of the surface roughness, $\sigma_{film\text{-}air}$, is different for organic and organic-inorganic films, and increases as a function of the number of layers (Fig. 1, inset), the behavior of the relative surface roughness, defined as $\sigma_{film\text{-}air}/D_{film}$, is nearly identical for all systems studied (Fig. 1).

The significant increase of the XRR-derived overall film thickness for the organic-inorganic films (in comparison with organic films) indicates the presence of relatively thick inorganic layers within the superlattices. The electron densities of the hybrid GaO_x and InO_x films having 4-5 layers are ~1.30 and ~1.65, respectively, as obtained from the fitting procedure. Such high electron densities confirm the presence of dense structures within the films (in contrast, the electron density of the all-organic **1**-based films is only ~0.30-0.34). Based on simple estimations, we conclude that the mass contribution of the inorganic part in Ga- and In-based SAS multilayers is about 50%.

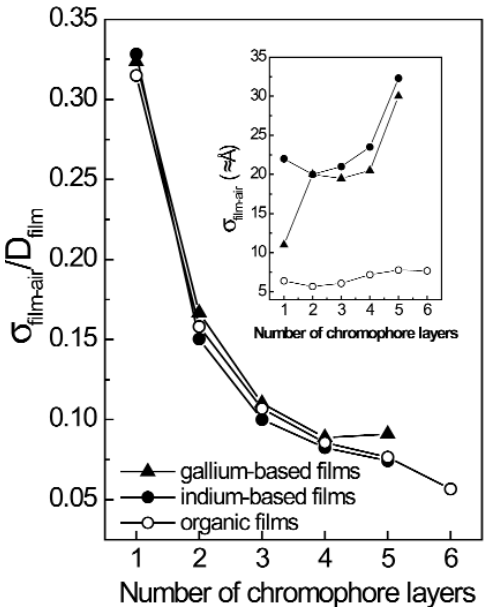

FIG. 1. Relative film roughness, $\sigma_{film\text{-}air}/D_{film}$, for organic films and for hybrid films with incorporated Ga and In oxides as functions of the number of chromophore layers. Inset: the film roughness as a function of the number of chromophore layers.

XRR analysis of multilayer electro-optic films containing a known chromophore and intercalated Ga or In metal oxide layers demonstrates an efficient approach to the assembly of organic and organic-inorganic hybrid superlattices having a variable electron density and therefore refractive indices tunable over a significant and useful range (1.52-1.84 at 650 nm). This solution-based deposition of Ga or In metal oxide layers is suitable for nanometer scale film construction with regular, vertical organization of the microstructure and makes possible tunable, metal-dependent modification of physicochemical properties.

Acknowledgments

This work was supported by the NSF under grants no. DMR-9978597 and DMR-0076077 (NSF MRSEC program), and by DARPA/ARO under contract (DAAd 19-00-1-0368). Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, under Contract No. W-31-109-ENG-38.

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