

Title	分子層堆積法を用いた橋かけ多層薄膜の合成
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ABSTRACT

The research of cross-linked organic thin films garnered much attention for its many conventional applications like organic thin film transistors, purification membranes and so on. However, the synthesis of thin films with nanometer scale is very challenging. One of the simple and versatile techniques to prepare nanometer scale cross-linked multilayer thin films is solution based molecular layer deposition (MLD). However, to fabricate organic thin films with MLD technique need to deal with several parameters: solid surface properties, self-assembled monolayer, monomers symmetrical combination, as well as optimized reaction condition. Any of the above mentioned parameters can make significance influences of films physical and chemical properties. In this research, I focused a unique monomers combination on fabricating thin films with 3D molecular networks.

In this thesis, synthesis of urea (bonded) cross-linked multilayer thin film was demonstrated by sequential deposition of bifunctional 1,3-phenylene diisocyanate (PDI) and tetrafunctional tetrakis(4-aminophenyl)methane (TAPM) molecular building blocks over Si/SiO₂ surface. Multilayer growth as a function of deposition cycles was inspected using UV-vis absorption spectroscopy. From infrared spectroscopy results, three characteristic infrared bands confirmed the formation of polyurea networks. X-ray photoelectron studies also unveiled the formation of polyurea networks. From X-ray reflectivity (XRR) density investigation, constant mass density was not observed with a number of deposition cycles. This difference in packing density might derive from the different degrees of cross-linking among layers proximate to the substrate surface and extending away from the substrate surface. Moreover, grazing incidence small-angle X-ray scattering (GI-SAXS) studies demonstrated the improvement of structural ordering with deposition cycles or film thickness.

However, by changing Si substrate surface characteristic by chemical etching and followed by oxygen plasma activation, a significant variation was observed in polyurea films mass density property, even though films show non-linear mass density behavior. This may happen due to the formation of the dense packed amine-terminate self-assembled monolayer (SAM), which is formed prior to the layer deposition. This dense packed self-assembled monolayer, reduced the initial or buffer layers packing density by forming a significant number of double reactions between surface attached amine groups and initial deposited 1,3-phenylene diisocyanate (PDI) monomer. However, film mass density is successively increased with layers deposition. This phenomenon resulted due to the presence of multi-functional TAPM monomer, which can laterally extend the molecular networks using multiple reactive sites. This result suggests not only the degree of cross-linking but also particular monomer combination is responsible for getting variable density property in multilayer thin films.

Keywords: Polyurea, Covalent linkage, Self-assembled monolayer, Layer-by-Layer, Mass density