

**MOLECULAR LAYER DEPOSITION OF POLY(P-PHENYLENE TEREPHTHALAMIDE)
FILMS USING TEREPHTHALOYL CHLORIDE AND PHENYLENEDIAMINE**

By

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This thesis entitled:

Molecular Layer Deposition of Poly(p-phenylene terephthalamide) Films Using Terephthaloyl
Chloride and Phenylenediamine

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The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

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Molecular Layer Deposition of Poly(p-phenylene terephthalamide) Films Using Terephthaloyl Chloride and Phenylenediamine

Thesis directed by Professor Steven M. George

Abstract

Ultrathin polymer films can be fabricated using the gas phase method known as molecular layer deposition (MLD). This process typically uses bifunctional monomers in a sequential, self-limiting reaction sequence to grow conformal polymer films with molecular layer control. In this study, terephthaloyl chloride (TC) and phenylenediamine (PD) were used as the bifunctional monomers to deposit poly(p-phenylene terephthalamide) (PPTA) thin films. 3-aminopropyl trimethoxysilane (APMS) or ethanolamine (EA) was used to functionalize the surface to prepare an amine-terminated surface prior to the PPTA MLD. The surface chemistry and growth rate during PPTA MLD at 145°C were studied using in situ transmission Fourier transform infrared (FTIR) spectroscopy experiments on high surface area powders of SiO₂ particles. PPTA MLD thin film growth at 145°C was also examined using in situ transmission FTIR experiments on flat KBr substrates with an amine-terminated Al₂O₃ ALD overlayer. The integrated absorbance of the N-H and amide I stretching vibrations was measured and used to determine the thin film thickness. X-ray reflectivity (XRR) experiments were also employed to measure the film thickness after PPTA MLD at 145°C and 180°C. The experiments revealed that TC and PD reactions displayed self-limiting surface chemistry. The surface species alternated with sequential TC and PD exposures and the PPTA MLD films grew continuously. However, the growth rates per MLD cycle were less than the ideal expectations and varied between 0.4-2.9 Å per TC/PD reaction cycle. The lower growth rates are explained by the growth of a limited number of polymer chains on the substrate. The variability in the growth rate is attributed to the difficulties with the bifunctional monomer precursors. Alternative surface chemistries for polymer MLD are proposed that would avoid the use of bifunctional monomers.

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I. INTRODUCTION

Atomic layer deposition (ALD) and molecular layer deposition (MLD) are thin film growth techniques that can deposit conformal and precise ultrathin films [1-3]. Both ALD and MLD are based on sequential, self-limiting surface reactions [2]. The chemical functionality of the surface species switches in a digital manner and approximately one atomic or one molecular layer is deposited during each surface reaction. ALD and MLD methods offer unprecedented control for inorganic and organic thin film growth. ALD and MLD techniques can also be used in combination to deposit hybrid inorganic/organic thin films.

There has recently been renewed interest in MLD. Since their introduction by several groups in Japan in the 1990s, MLD methods have been based on bifunctional monomer precursors such as A-L-A and B-M-B. In these precursors, "A" and "B" are chemical functional groups and "L" and "M" are organic fragments. MLD growth has been demonstrated for a variety of organic polymers such as polyamide [4], polyimide [5], polyimide-polyamide [6] and polyurea [7]. A cartoon illustrating the MLD approach is shown in Fig. 1.

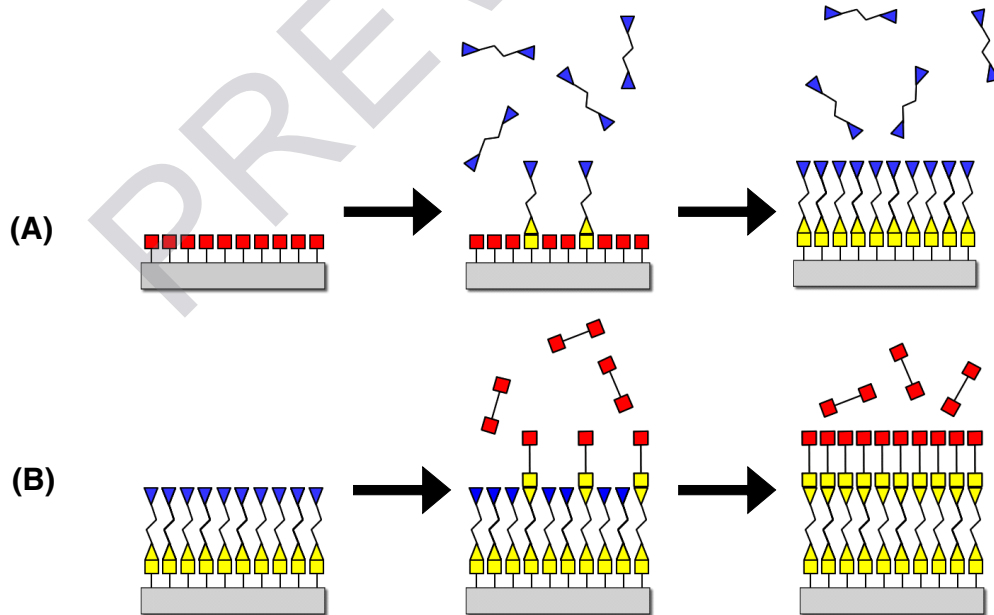


Figure 1. Schematic of molecular layer deposition (MLD) method.