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Covalent molecular assembly: Construction of ultrathin multilayer films by a two-dimensional fabrication method

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ABSTRACT

A two-dimensional fabrication method was employed to assemble ultrathin multilayer films with specific three-dimensional structures by making use of interlayer and intralayer covalent bonding. The films were assembled in a layer-wise fashion on a silicon surface using bi- and multi-functional molecules as building blocks and strengthened by lateral cross-linking. The fabrication process could be controlled at the sub-nano-scale with the roughness of the surface after deposition of each layer within 0.2 nm. The film showed better resistance to harsh environments than randomly cross-linked or linearly linked films of comparable thickness. The combination of covalent LbL assembly and lateral cross-linking has significant potential as a method of fabrication for assembling nano-structures for a variety of applications.

1. Introduction

Ultra-thin multilayer films have attracted substantial interest recently due to their many applications, such as surface protection [1], membrane modification [2,3], drug delivery [4,5], and bio-sensors [6,7]. Layer-by-layer (LbL) self-assembly is a simple and versatile method to fabricate ultra-thin multilayer films with controlled thickness and composition. In LbL assembly, the molecules are adsorbed and assembled on the substrate through different interactions, such as physical adsorption, electrostatic interaction [8–10], hydrogen bonding [11,12], charge-transfer interaction [13], and metal–ligand interaction [14,15]. This deposition process can be repeated numerous times until desired number of films and thickness are obtained. Functional molecules and nanoparticles can also be incorporated thereby enabling utilities such as antibacterial protection [16] and electrochromism [17], nano-sensors [18], and nano-reactors [11,19,20]. Despite their extensive usage and potential applications, stability of multilayer films is not satisfactory due to the fragility of the inter- and intra-layer bondings. Typically, the different layers are held together by weak intermolecular interactions, and they can be solved by organic solvent or be destroyed in high pH solution [21], which will limit their applications.

Cross-linking is a convenient and effective way to strengthen the multilayer films. Many approaches have been attempted to induce cross-linking reaction in the multilayer films. Zhang and Cao [13] built a cross-linked charge-transfer multilayer film containing diazo resin by UV irradiation, which was stable in polar solvents. Shao et al. [22] fabricated a long-lifetime light-emitting multilayer film by thermally-induced cross-linking. Stable free-standing multilayer films strengthened by catalyst [23] and electron beam [24] induced cross-linking reactions were obtained by peeling them from the substrate in H_2O/DMF/$ZnCl_2$ and HF, respectively. Photo irradiation was also frequently used to induce cross-linking in both multilayer [25] and monolayer films [26]. Cross-linking improves the intrinsic strength of the multilayer films; however, the interactions between the multilayer films and the substrate are still weak due to their non-covalent properties [22,24], which could limit the applications of functional multilayer films. Therefore, there is a need for improving assembly techniques that may involve intra-layer as well as layer-to-layer links. Furthermore, versatile three-dimensional structures that cater to stability and architectural requirements are desired for construction of nanodevices that may need many assembly steps.

Covalent LbL assembly [27,28] is a powerful method to fabricate stable multilayer films in which covalent binding serves as the driving force for molecular assembly. Similar to the concept of click chemistry [29], but more versatile, covalent LbL assembly is a simple method to build nanostructures efficiently without the need for isolation of the product. The multilayer films can be stable in harsh environments due to the strong binding between different layers and between the film and the substrate. This stability facilitates treatment of films to remove weakly adsorbed or physisorbed molecules [30], thereby giving rise to more precise and ordered structures. Furthermore, the films not only can be used to immobilize

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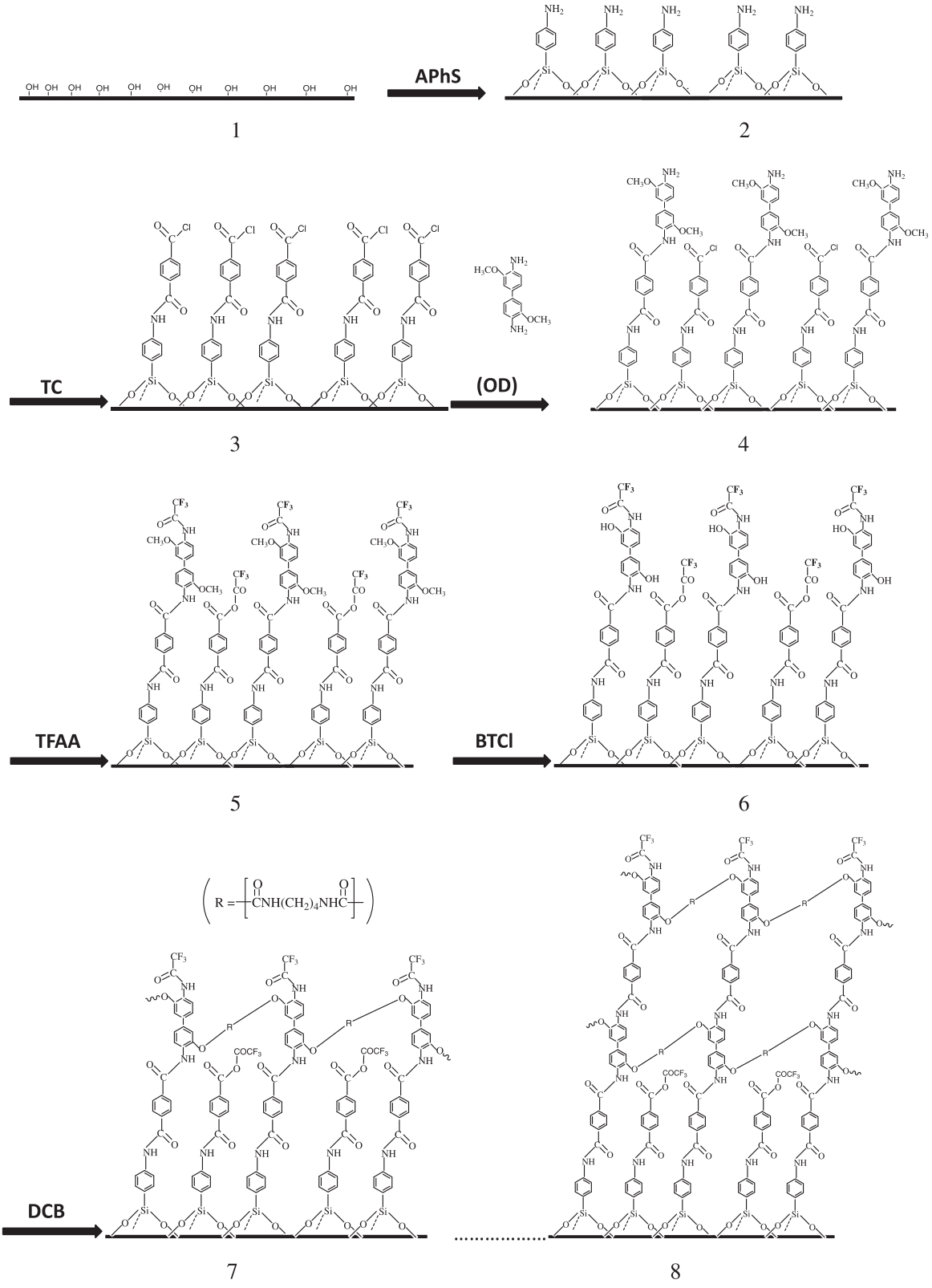

Scheme 1. Fabrication process of lateral cross-linked multilayer films 1: surface of silicon wafer; 2: after deposition of APhS; 3: after deposition of TC; 4: after deposition of OD; 5: after deposition of TFAA; 6: after demethylation reaction; 7: after cross-linking reaction (LCMF1); 8: multilayer film with two cross-linked layers (LCMF2).

functional molecules [31], but also could endure further reactions during the additional manipulations.

To provide additional robustness, covalent multilayer films can be further strengthened by cross-linking. Furthermore, cross-linking could be used as a structural fabrication tool. In addition to the vertical fabrication of LbL assembly by interlayer covalent binding, cross-linking reactions at specific layers can be regarded as a lateral fabrication process. A combination of vertical and lateral fabrication could be a feasible method to fabricate complex devices with three-dimensional structures. The enhanced stability pro-