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Self-Assembly of Zirconium N, N′-bis(benzyl phosphonic acid)-3,4,9,10-Perylene bis(dicarboximide) Multilayer Films on Silicon and Quartz Substrates

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Asymmetric multilayers of zirconium N,N'-bis(benzyl phosphonic acid)-3,4,9,10-perylenebis(dicarboximide) (Zr-BPPI) molecule are prepared on modified silicon and quartz substrates. The substrates were functionalized with phosphorous oxychloride to have a phosphonic acid on substrates. Mono- and multilayer structures are then prepared by alternately adsorbing zirconium ion and BPPI from an aqueous solution. The characteristics of multilayer films were studied by ellipsometry, UV-visible absorption and cyclic voltametry. Ellipsometry and UV-visible absorption measurement confirmed the layer-by-layer growth of the film.

Keywords: self-assembly, Zr-BPPI multilayer, UV, ellipsometry

INTRODUCTION

Recently, self-assembled mono- and multilayer formed on solid substrates have generated considerable interest because of the potential of controlling the molecular architecture and chemical and physical properties (photoconductors, photovoltaics, electrochromics, and nonlinear optical elements) of layered assemblies on surfaces. Especially, the transition metal phosphonates multilayer films on surfaces provide an attractive means of constructing thermally and

sovolytically stable films of controlled thickness consisting of spatially well-defined molecular components[1-2]. In this study, we report the preparation of multilayer of zirconium N,N'-bis(benzyl phosphonic acid)-3,4,9,10-perylene bis(dicarboximide)(Zr-BPPI) based on the sequential adsorption of metal ion and bisphosphonic acid and the characterization of the mutilayer structure using UV-visible absorption measurement, ellipsometry, and cyclic voltametry. The perylenedicarboximide derivatives have been well known as photoconducting materials in xerography[3-6]. The photoconductivity of BPPI comes from the strong $\pi-\pi$ interactions between fused aromatic ring structures.

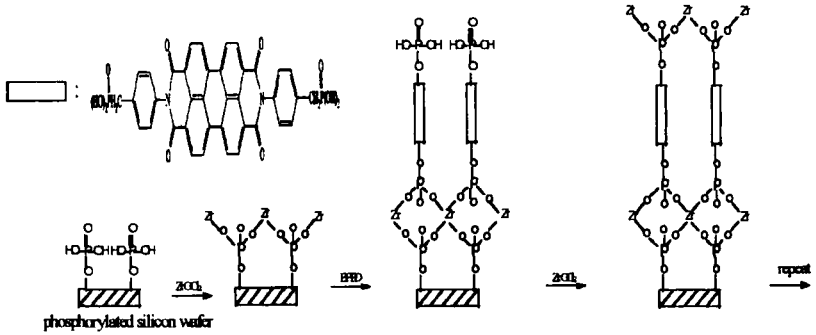

FIGURE 1. Synthetic scheme for the formation of Zr-BPPI multilayers.

In the multilayer structure of Zr-BPPI presented here the adjacent perylene chromophore in each layer can be stacked each other parallel to the substrate as shown schematically in Figure 1. Therefore we can expect a directional photoconductivity in this multilayer film.

EXPERIMENTAL

MEASUREMENT AND SYNTHESIS OF BPPI

UV-visible absorption spectra of Zr-BPPI films were obtained on a HP 8452A

diode array spectrometer. Ellipsometry measurements were performed on a Rudolph Auto-EL2 ellipsometer using 632.8 nm radiation from halogen lamp. The electrochemical measurement was carried out in an argon-purged one-compartment cell, equipped with a platinum counter electrode and SCE reference electrode. The cyclic voltammetry was measured using a EG & G PAR 263A potentiostat. Spectroelectrochemical measurements were performed with a conjuction of Hitachi U-3210 spectrophotometer and PAR 263A potentiostat. BPPI was prepared from the condensation reaction of 3,4,9,10-perylemedicarboxylic dianhydride and 4-aminobenzyl phosphonic acid, which is preapared from acid hydrolysis of diethyl 4-aminobenzyl phosphonate, in a molten imidazol with zinc acetate at 170℃.

PREPARATION OF Zr-BPPI FILMS

Zr-BPPI films were grown using methodology developed by Katz[7-8]. The substrates were rinsed with acetonitrile and then phosphorylated by treatment with an acetonitrile solution of $POCl_3$ and 2,4,6,-collidine(10 mM in each) for 12h at 80℃. The substrates were zirconated in a 5 mM solution of $ZrOCl_2$ for 3h at room temperature. Multilayers of Zr-BPPI were produced by alternate dippings in 5 mM BPPI and $ZrOCl_2$ solution at room temperature for 1h.

RESULTS AND DISSCUSION

Figure 2(a) and Figure 2(b) show the UV absorbance of Zr-BPPI multilayer and the thickness of BPPI multilayer films as a function of the number of layers. As the number of layers increased, the absorbance of the film increasedlinearly. While the assumption that the initial Zr-BPPI layer has the same index

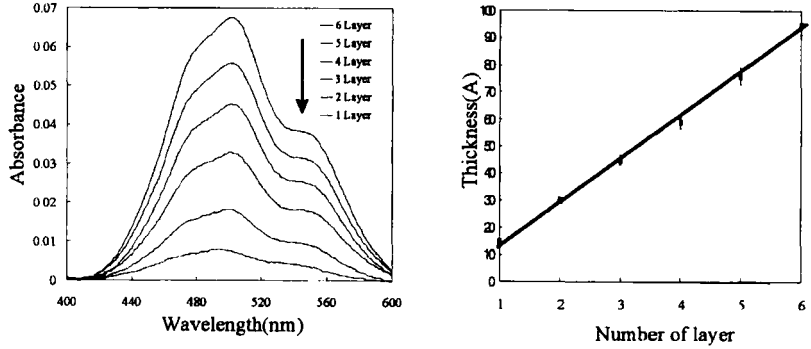

FIGURE 2. (a) Measured absorbance of Zr-BPPI deposited on a quartz plate, (b) Thickness of Zr-BPPI multilayer films as a function of the number of layers calculated from ellipsometry data.

of refraction as the subsequent multilayer film might not be physically valid, the ellipsometrically determined thickness is nearly independent of the index of refraction and this will not be a significant source of error. The slope of the line, which means average thickness of layer, is 15.8Å/layer. The straight-line behavior indicates that individual layers are uniform in average thickness. Figure 3 shows cyclic voltamogram of BPPI layer on TiO_2. The quarsi-reversible peaks are systematically increased as the numbers of layer increase. Control experiments showed that redox peaks do not increase without treatment of zirconyl chloride solution in each layer-growing step. As the layers grow, the integrated charges of cathodic peaks after background substraction are almost linearly increased (not shown here). It means that the adsorbate concentration in each layer is constant. The heterogeneous electron transfer from the

conduction band of TiO_2 to the Zr-BPPI multilayers has been observed by cyclic voltammetry.

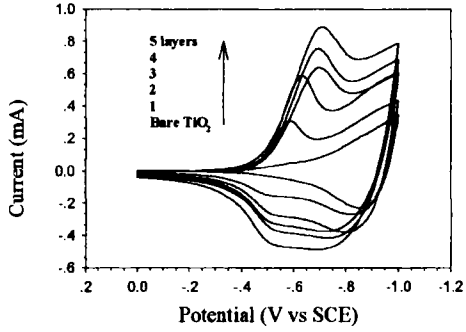

FIGURE 3. Cyclic voltamogram of BPPI layer on TiO_2.

CONCLUSION

Ellipsometric measurements have shown a linear increase in total film thickness as a function of the number of layers deposited and UV-vis spectroscopic studies of the deposition process are consistent with the ellipsometric results. The average thickness of the film derived by ellipsometry is about 15.8Å. Also, the quarsi-reversible peaks of cyclic voltamogram are systematically increased as the numbers of layer increase. These results indicate that the same amount of BPPI layer is placed on the substrate after each deposition cycle.

Acknowledgment

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