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The Photochemical Characterization of Zirconium N,N′-Bis(ethyldihydrogenphosphate)-3,4,9,10-perylene(dicarboximide) Multilayers on Silicon Surface

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The N,N'-bis(ethyldihydrogen phosphate)-3,4,9,10-perylene(dicarbox -imide) (EPPI) have been well known as photoconducting materials in xerography and as photoinduced electron transporting materials. We describe its spectral properties in solution and self-assembled zirconium-EPPI multilayer on quartz substrate. Also, the orientation of EPPI molecules, the intermolecular interactions between EPPI molecules and layer formation was interpreted.

Keywords Self-assembled film; Photochemcal property; PL spectra

INTRODUCTION

Self-assembled thin films onto solid substrates have generated considerable interest recently because of the potential for controlling the molecular architecture and chemical and physical properties of layered assemblies on surface. Among this self-assembled film, the preparation of zirconium phosphonate multilayer films on silicon and gold has been elucidated using a variation of the self-assembling technique. Especially, the thermal and photochemical stability of the self-assembled perylene derivatives film with their photoactive and photoconductive properties make this class of π-conjugated organic chromophore attractive candidates for a number of industrial applications[1]. In our study, we use the N,N'-bis(ethyldihydrogen

phosphate)-3,4,9,10-perylene(dicarboximide)(EPPI) which have been also known as photoinduced electron transporting materials and have

FIGURE 1. Molecular structure of EPPI

very stable architecture with Zr^{4+} ions. The molecular structure of EPPI is shown in Figure 1. In this study, we report multilayer synthesis based on the sequential adsorption of components and characterization of self-assembled Zr-EPPI multilayer film on modified surface. The orientation of EPPI molecules, the intermolecular interactions between EPPI molecules and layer formation was interpreted.

EXPERIMENTAL

Cleaned substrates were phosphorylated with $POCl_3$ and 2,4,6-collidine in acetonitrile solution for 12 hours at 70℃. Si wafer and quartz produced in this way were dipped in 5 mM $ZrOCl_2$ solution and 1 mM EPPI in KOH aqueous solution at room temperature, alternatively [2]. Ellipsometric measurements were carried out using a Rudolph auto-EL II ellipsometer using halogen lamp (632.8 nm), at an angle of incidence $\phi = 70°$. UV-Vis spectra were obtained by using HP8452A diode-array spectrophotometer. PL spectra were recorded on an ISS PC1 spectrofluorometer.

RESULTS AND DISCUSSION

Characterization of self-assembled Zr-EPPI multilayer. The growth and characterization of self-assembled Zr-EPPI multilayer film have been studied in detail. The EPPI molecules were incorporated into Zr-EPPI multilayer as an electron donor and existed in the state of EPPI n-mer in a concentrated solution and solid film. Figure 2(a) shows the UV-Vis spectra of the EPPI solution and the self- assembled Zr-EPPI film. The π - π * absorption bands of EPPI monomers and EPPI n-mers in the EPPI solution and self-assembled Zr-EPPI film is appeared at 472 nm and 496-498, 538-548 nm. The π - π * absorption band of EPPI monomers at 472 nm were appeared in EPPI solution and weren't appeared in Zr-EPPI film. The absorption bands of EPPI n-mers and absorption bands by intermolecular interactions between EPPI n-mers

were appeared at the longer wavelength, 496-498 nm and538-548 nm.

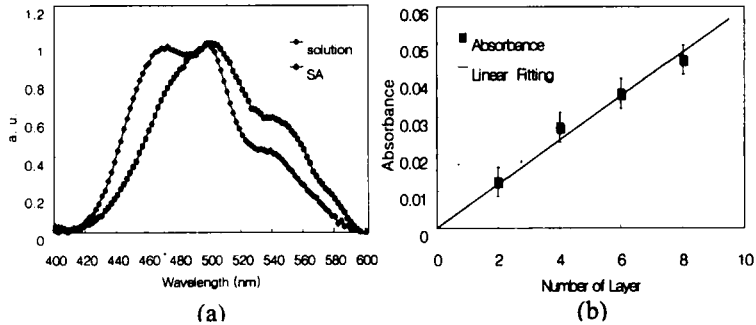
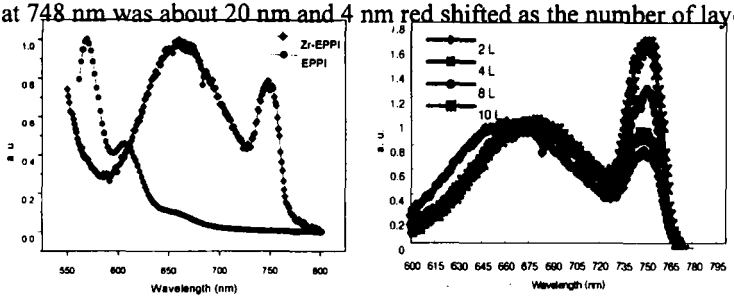


FIGURE 2. (a) UV-vis spectra of EPPI solution and self-assembled Zr-EPPI film (b) Linear fitting of the absorbance of Zr-EPPI multilayer films as a function of the number of layers

The absorption band of Zr-EPPI film was red shift about each 2 nm and 10 nm comparing to that of EPPI solution. These results mean that the distance between EPPI monomers is shorter because the free molecules of EPPI solution were packed into solid film. Figure 2(b) shows the plot of absorbance of Zr-EPPI multilayer films as a function of the number of layers at maximum wavelength, 498 nm. The absorbance of the film increases linearly as the number of layers increases at 498 nm. The linear increase in absorbance indicates that the same amount of EPPI molecules is being deposited in each treatment. Also, ellipsometric data are a better indication of uniformity and complete coverage since it measures an average thickness. As the number of layers increases, the thickness of the film increases linearly (as not shown here). The slope of the line gives a layer thickness of 13.03 Å/layer. PL spectra of EPPI solution and self-assembled Zr-EPPI layer give us the information of structural order how the EPPI molecules was oriented in the EPPI solution and on the self-assembled Zr-EPPI layer. Figure 3(a) shows the emission (λ_{exc}= 498 nm) spectra of EPPI solution and self-assembled Zr-EPPI layer. The PL spectrum of self-assembled Zr- EPPI layer showed two peaks at 660 nm and 748 nm, which is about 70 nm and 100 nm red shifted. The red shifts probably result from the increment of π - π^* interactions between EPPI molecules because the EPPI molecules were packed onto the solid Zr-EPPI layer. The excimer peak at the 748 nm means that the distance between EPPI molecules is very short enough to make the EPPI n-mers. Figure 3(b) shows the normalized emission spectra of self-assembled Zr-EPPI layer

as the number of layer increase. The peak at 660 nm and excimer peak at 748 nm was about 20 nm and 4 nm red shifted as the number of layer



(a) (b)

FIGURE 3. (a) Emission (λ_{exc} = 498 nm) Spectra of self-assembled Zr-EPPI layer and EPPI solution. (b) Emission Spectra of the film in various layer

increased. The intensity of excimer increased as the number of layer increased. These results indicate that the intra- and intermolecular interaction onto the self-assembled Zr-EPPI layer increase between EPPI molecules of a layer and different layer, EPPI molecule and EPPI molecule at the same layer.

CONCLUSIONS

The self-assembled Zr-EPPI multilayer film was formed on the modified silicon and quartz substrates. UV, ellipsometry, PL spectrometer did the characterizations of this film. The linear fitting plot of thickness and UV-vis absorbance shows that the Zr-EPPI film grows very well. The average thickness of Zr-EPPI 1 layer is 13.03 Å. Also, the EPPI molecules onto the self-assembled Zr-EPPI layer were packed, comparing the PL spectra of EPPI solution with the PL spectra of self-assembled Zr-EPPI layer.

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REFERENCES

[1]. H. Lee, L. J. Kepley, H. G. Hong, T. E. Mallouk, ~~*J. Am. Chem. Soc.*~~, **110**, 618 (1988).

[2]. H. J. Chae, Y. I. Kim, H. Lee, ~~*Bull. Kor. Chem. Soc.*~~, **19**, 27 (1998).