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# Optical Characteristics of Self-Assembled Ultrathin Films of Tetra-Copperphthalocyanine by Attenuated Total Reflection

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Multilayer thin films consisting of alternate layer-pairs of cationic macrocycles (tetra-copperphthalocyanine) and anionic macromolecules (polyethylenimine) were fabricated on thin silver film using alternate electrostatic self-assembly technique. The optical properties of the film were characterized by uv-vis absorption spectra and attenuated total reflection measurements. From the data analysis based on the multilayer reflection theory, it was shown that the ultra thin films were successfully fabricated by self-assembly technique with the mean layer-pairs thickness of 25 Å. Moreover, especially for tetra-copperphthalocyanine layer, we obtained the anisotropy in dielectric constants with respect to the surface normal, indicating anisotropic orientation of the tetra-copperphthalocyanine molecules on the polyethylenimine layer.

Keywords self-assembly; tetra-copperphthalocyanine; attenuated total reflection ; polyethylenimine

## INTRODUCTION

Fabrication of multilayer thin films has attracted considerable interest for their use in the area of optical waveguides and integrated optical devices.[1] Langmuir-Blodgett (LB) technique and self-assembly (SA)

method have been frequently used for constructing the ultra-thin film devices.[2] The SA method is used to fabricate multilayered structures in a layer-by-layer manner through the Coulomb force between the opposite charges. In the SA films, the structural, chemical, and physical properties of the multilayers are complicated and not fully understood, yet. There have been around a variety of methods to characterize the SA films in the fabrication of multilayered structure. In the present work, we have fabricated a multilayer ultrathin film using SA method and investigated the structural properties of the films by employing optical means such as the uv-vis absorption spectra and the attenuated total reflection (ATR) reflectance[3-5] which is known as a sensitive tool in characterizing the surfaces and interfaces.

## EXPERIMENTAL

We fabricated the electrostatic alternate self-assembled multilayers of macrocycle of anionic tetra-copperphthalocyanine (Tetra-CuPc) and macromolecule of cationic polyethylenimine (PEI, Mw:25000), whose structures are shown in elsewhere.[6] The silver (Ag) thin films with the thickness of ~400 Å were thermally evaporated on the BK7 substrates. The silver-coated substrates were immersed into 2.5 mM solution of positively charged PEI for 20 min. Because positively charged PEI polymers are attracted to the silver surface, a monolayer of PEI will spontaneously disperse on the substrate. The PEI coated substrates were washed with deionized water to ensure that all the nonadsorbed materials were removed, and dried in a stream of $N_2$ gas. Next, the PEI-coated substrates were immersed into 0.07 mM solution of Tetra-CuPc for 20 min., followed again by rinsing with deionized water and drying in a stream of $N_2$ gas. After one dipping cycle, a layer-pair of PEI and Tetra-CuPc was formed on the silver surface. Additional layer-pairs were deposited to form a multilayer by alternately dipping the sample in solutions of PEI and Tetra-CuPc.

## RESULTS AND DISCUSSION

The growth of multilayer thin films was monitored by measuring the uv-vis absorption spectra and ATR reflectance, as shown in Fig. 1(a). The optical absorption, as shown in inset of Fig. 1(a), increases linearly as the increasing number of layer-pairs of PEI/Tetra-CuPc, indicating the linear increase in the thickness of the layer-pairs. In the ATR curves measured from the Ag, Ag/PEI, and Ag/PEI/Tetra-CuPc SA films, the surface plasmon excitations between the silver - film interfaces are clearly observed as indicated by a sharp decrease in the reflectance at the resonant angle (Fig. 1(b)). The solid line in Fig. 1(b) shows the theoretical least-square fit of the multilayer Fresnel reflection, which is in good agreement with the experimental data. From the fit, the thickness $d$ and complex dielectric constant ( $\varepsilon_R + i\,\varepsilon_I$ ) of each layer were determined; $d$ = 399.7 Å and $\varepsilon = -17.164 + i\,0.808$ for Ag film and $d$ = 13.4 Å and $\varepsilon = 2.397 - i\,0.414$ for PEI. For the Tetra-CuPc layer, two components of the dielectric constant with respect to the surface normal ($\varepsilon_\perp$) and the surface parallel ($\varepsilon_\parallel$) were introduced to describe the planar orientation of Tetra-CuPc molecules on the PEI

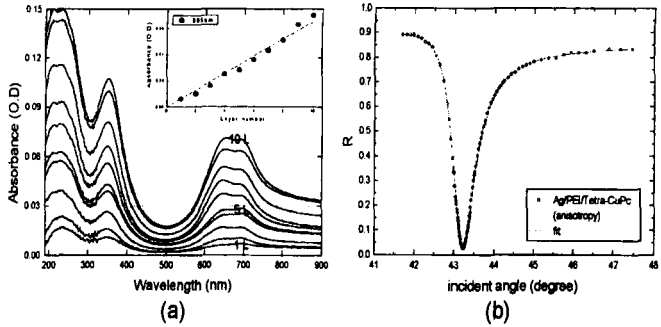


FIGURE 1 (a) The optical absorption spectra of the PEI/Tetra-CuPc SA film on a fused quartz substrate. (b) The ATR curves of the layer-pair of PEI/Tetra-CuPc on silver film.

surface. It is founded that $\varepsilon_{\parallel} = 2.092 - i\ 0.041$ is larger than $\varepsilon_{\perp} = 1.366 + i\ 0.949$ with $d$ = 12.2Å, indicating the macroscopic optical anisotropic response of the Tetra-CuPc monolayer. This observation provides the structural information that the orientationl distribution of Tetra-CuPc molecules, electrostatically adsorbed on the isotropic PEI surface, is strongly anisotropic. From these the thickness of layer-pair of PEI/Tetra-CuPc was estimated to be about 25.6Å.

## SUMMARY

We investigated the optical characteristics of electrostatic SA films consisting of alternate layer-pairs of cationic Tetra-CuPc and anionic PEI on the thin silver film. From the data analysis, it was shown that the mean layer-pairs thickness of the fabricated SA films is ~ 25Å. The absolute values of the complex dielectric constant of the each layer were also determined from the ATR curves. Moreover, for the Tetra-CuPc monolayer, the observed dielectric anisotropy with respect to the surface normal strongly indicates the in-plane orientation of the Tetra-CuPc molecules in the monolayer.

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**References**

[1] P. Smolenyak, R. Peterson, K. Nebesny, M. Torker, D. F. O'Brien, and N. R. Armstrong, J. Am. Chem. Soc. **121**, 8628 (1999).
[2] P. M. Kimura et. al., Langmuir **16**, 2076 (2000).
[3] W. Knoll, Annu. Rev. Phys. Chem. **49**, 569 (1998).
[4] G. J. Sprokel, Mol. Crst. Liq. Crst. **68**, 39 (1981).
[5] E. Kretschmann, Z. Physik, **241**, 313 (1971).
[6] B. N. Achar, G. M. Fohlen, and J. A. Parker, J. Polym. Sci.: Polym. Chem. Edit., **20**, 1785 (1982).