# Ellipsometry, XRR, and GCIB-TOF-SIMS Analysis of Small Molecule Layers in Solution Process and Vacuum Deposition Process

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## ABSTRACT

*Ellipsometry, XRR, and GCIB-TOF-SIMS are applied to investigation of the spin-coating process as comparison of spin-coated samples and vacuum evaporated samples. The residual solvent of spin-coating process was observed in spin-coated samples by GCIB-TOF-SIMS. The result suggested that it can cause the decrease of refractive index observed in ellipsometry.*

## 1. EXPERIMENT

### 1.1 Sample preparation

We prepared 2-layer samples of PEDOT: PSS (poly(3,4-ethylenedioxythiophene): polystyrene sulfonate) and NPD (4,4'-di(1-naphtyl)-4,4'diamine). PEDOT:PSS was spin-coated on glass substrate at 2000 rpm for 60 sec and annealed at 200 °C for 10 min. NPD was deposited on PEDOT:PSS by vacuum deposition or spin-coating. The condition of spin-coating is 2000 rpm for 30 sec and annealed at 80°C for 5 min with 3 different solvents; dichloromethane (DCM), tetrahydrofuran (THF), cyclopropanone (CP). NPD monolayer samples on glass substrates are prepared as reference samples.

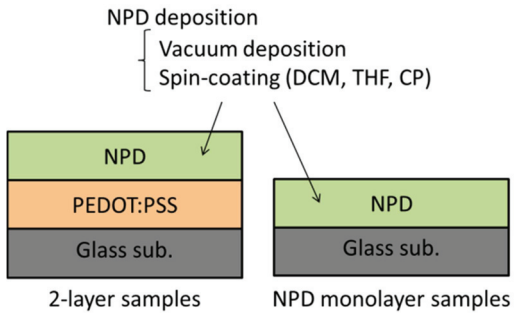


**Fig. 1 Layer structure of samples.**

### 1.2 Measurement conditions

X-ray diffractometer, SmartLab (Rigaku Corporation), was used for X-ray reflectivity analysis. TOF-SIMS depth profiles with GCIB cluster etching ion beam were measured by a TOF-SIMS apparatus (TOF.SIMS 5, ION-TOF GmbH, primary ion: $Bi_3^{++}$, etching ion: $Ar_{1600}^{+}$).

## 2. RESULTS AND DISCUSSION

### 2.1 Spectroscopic ellipsometry

Wavelength dependence of refractive index and extinction coefficient in the 2-layer samples (Glass/PEDOT:PSS/NPD) measured by ellipsometry are shown in figure 2.

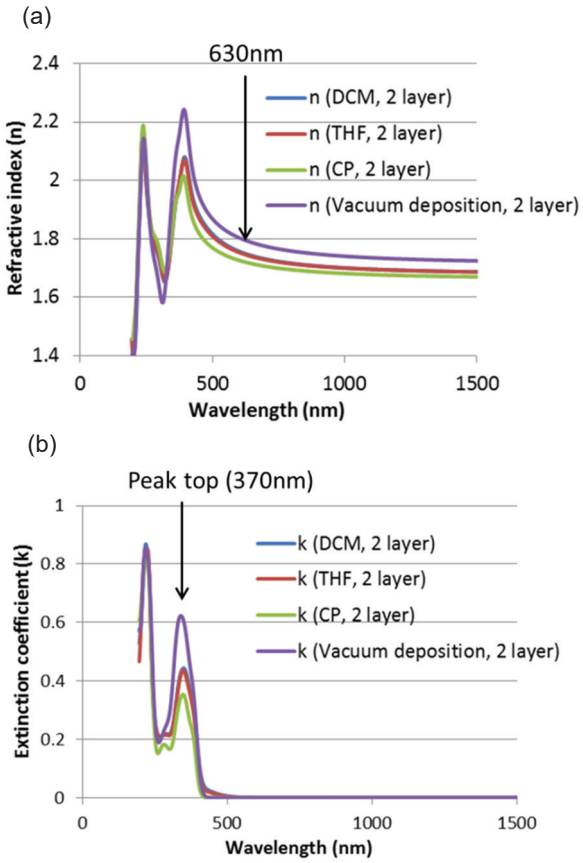


**Fig. 2 Wavelength dependence of refractive index and extinction coefficient in the 2-layer samples measured by ellipsometry.**

Refractive index in 630 nm and extinction coefficient in 370 nm as peak top are summarized in figure 3(a). The refractive index and the extinction coefficient were

both lower in the spin-coated samples than the vacuum-deposited sample and slightly different between different solvents. Even in the monolayer samples (Glass/NPD), similar tendency was observed (figure 3(b)). Therefore, These tendencies are caused not by the PEDOT:PSS layer but by the spin-coating process. Generally, refractive index correlates to density and polarizability of layer. Either of them contributed to the different of the refractive index between the samples.

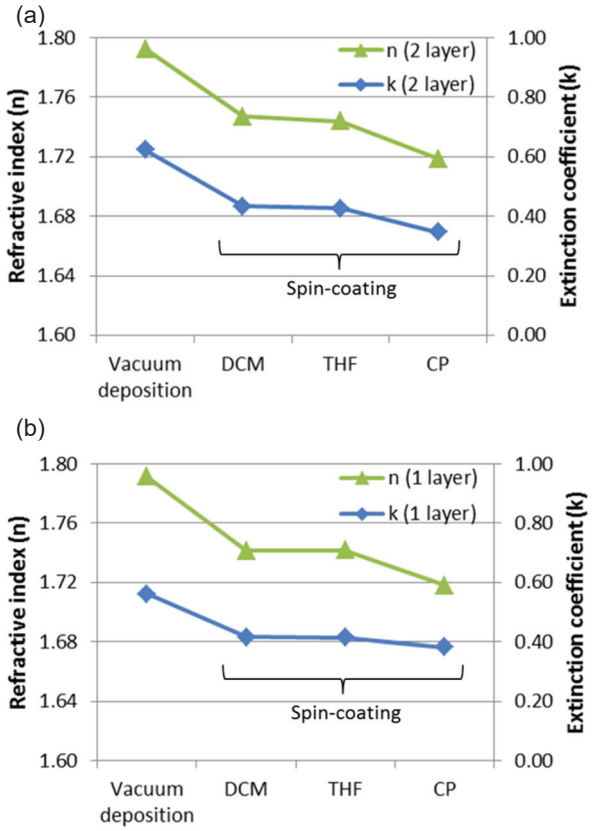


**Fig. 3 Refractive index and extinction coefficient of NPD in (a) 2-layer samples and (b) monolayer samples measured by ellipsometry.**

### 2.2 X-ray reflectivity (XRR)

Thickness and densities of layers in 2-layer samples measured by XRR are shown in figure 4(a). Surface layer with higher density than NPD layer was observed in the spin-coated samples. Although similar surface layer was observed in the vacuum deposited samples, the difference of the density from NPD layer was much smaller. The densities of NPD layers were almost same between samples. Even in the monolayer sample (Glass/NPD), similar tendency was observed (figure 4(b)). Therefore, the difference of the refractive index of NPD layers derived in ellipsometry was suggested to be caused by the difference of the polarizability between the samples.

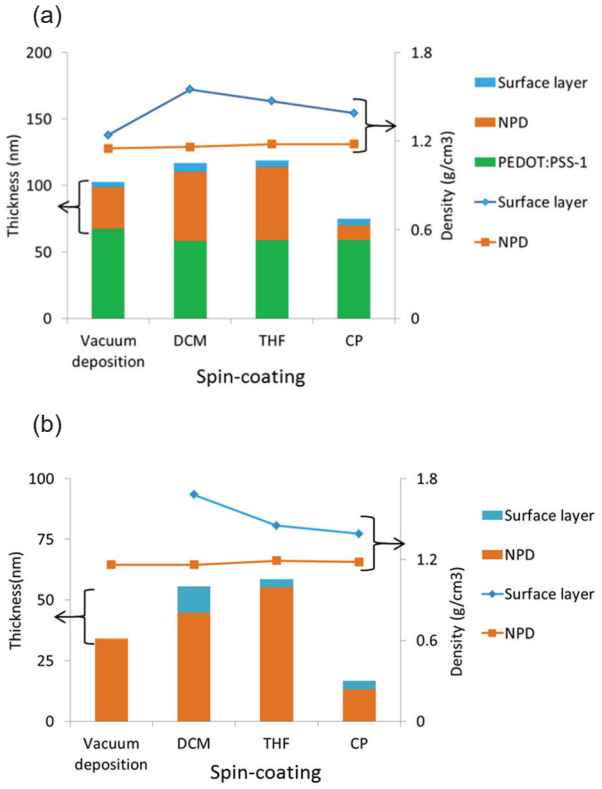


**Fig. 4 Thickness of layers and density of NPD layer in (a) 2-layer samples and (b) monolayer samples measured by XRR.**

### 2.3 Time-of-flight secondary ion mass spectrometry depth profiling with gas cluster ion beam (GCIB-TOF-SIMS)

Figure 5(a) is the overlaid depth profile of PEDOT:PSS observed by GCIB-TOF-SIMS. X axes of profiles were shifted to match interfaces of NPD and PEDOT:PSS between samples. We compared degree of diffusion of PEDOT:PSS into NPD layer by using intensities of $S^-$, $SH^-$, $C_2HS^-$ at the middle of NPD layer to minimize interference from other components.

The profile shapes of interface of layers were similar between the vacuum-deposited sample and the spin-coated samples. These peaks derived from PEDOT:PSS were slightly detected in NPD layers, and the spin-coated sample with THF was higher than the other samples. Therefore, component of PEDOT:PSS was slightly diffused into NPD layer in spin-coating process with THF.

Figure 5(b) is the overlaid depth profile of NPD. The profile was similar between the vacuum-deposited sample and the spin-coated samples. Therefore, Diffusion of NPD into PEDOT:PSS layer was not observed even in spin-coating process.

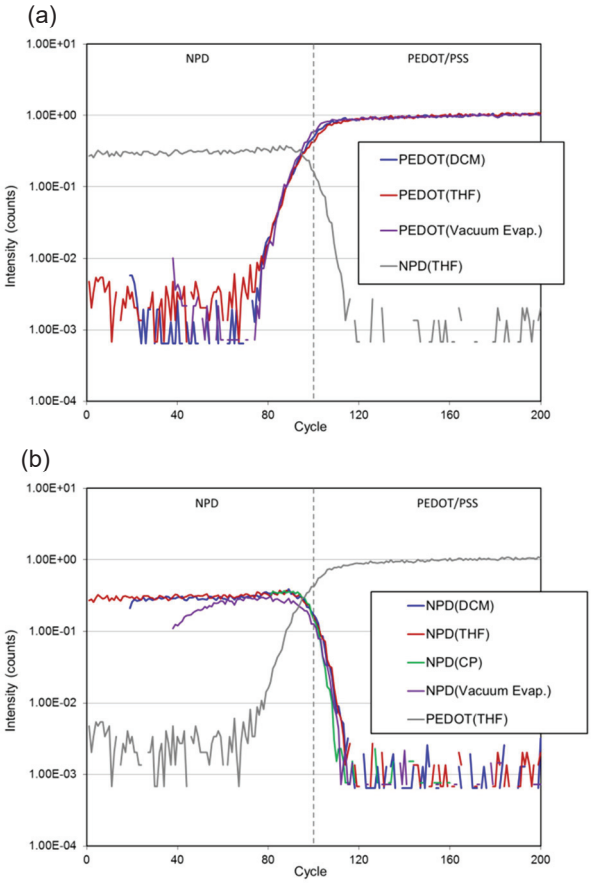


**Fig. 5 Overlaid depth profile of (a) PEDOT and (b) NPD in 2-layer samples measured by GCIB-TOF-SIMS; The peaks of PEDOT are $S^-$, $SH^-$, $C_2HS^-$ and that of NPD is $C_{38}H_{27}N_2^-$.**

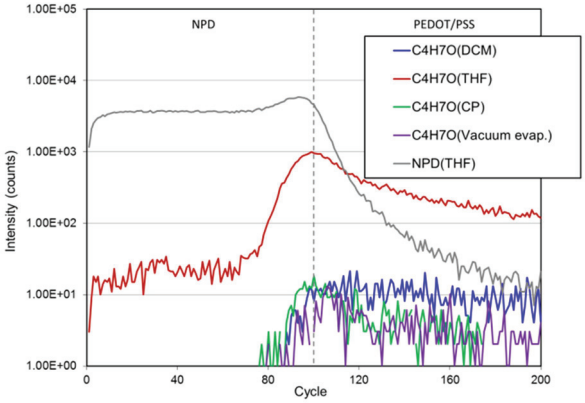


**Fig. 6 Overlaid depth profile of THF-related peak, $C_4H_7O^+$, in 2-layer samples measured by GCIB-TOF-SIMS. The peak of NPD is $C_{44}H_{32}N_2^+$.**

Overlaid depth profile of THF-related peak, $C_4H_7O^+$, in 2-layer samples is shown in figure 6. THF related peak was much higher in NPD layer and PEDOT:PSS layer of the spin-coated sample with THF than in those of the other samples. Therefore, THF related compound was detected as the residue after the spin-coating and the annealing process. Similar peak from residual solvent was detected in spin-coated sample with CP. Because these solvents are easily volatilized in TOF-SIMS instrument of ultra–high-vacuum instrument, these residual solvents were assumed to have stable state to high vacuum, such as decomposed compounds or salts. These residues changed the polarizability of NPD layer, which can cause the difference of refractive index derived in ellipsometry.

Figure 7 shows depth profile of other impurities of the spin-coated sample with THF. Sodium ($Na^+$) and aliphatic hydrocarbon ($C_4H_7^+$) are detected at the surface of NPD layer. These may be components of surface layer observed in XRR.

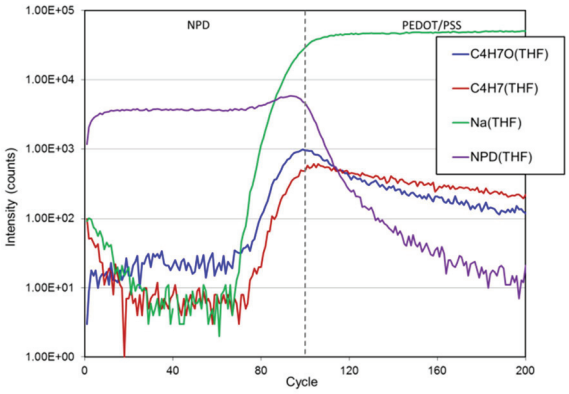


**Fig. 7 Depth profile of impurities in spin-coated sample with THF.**

## 3. CONCLUSION

The refractive index and the extinction coefficient measured by ellipsometry are lower in the spin-coated samples than in the vacuum deposited sample. The densities of NPD layers of samples measured by XRR coincided with each other. Slight diffusion of PEDOT:PSS was observed in the spin-coated sample even with organic solvents. Solvents used in spin-coating process or its decomposed compound were detected in NPD layer and PEDOT:PSS layer by GCIB-TOF-SIMS as the residue after the annealing. These impurities in NPD layer can cause the change of the polarizability and the refractive index.

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