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# ELECTROSPRAY DIALYSIS FOR INTERNAL COMPONENT IMAGING OF NANO-SIZED SAMPLES

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Various microstructure is needed for semiconductor products and pharmaceutical products, and the analysis techniques for microstructures are also required. For the precise analysis of microstructure, these analysis techniques must have high performances such as a high spatial resolution, a low detection limit, chemical information and so on. X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative analysis technique that measures the elemental composition and chemical state. But it is difficult that XPS of chemical imaging perform high resolution analysis and analyze the local information of materials. And, Ga focused ion beam time-of-flight secondary ion mass spectrometry (FIB-TOF-SIMS) is one of the high resolution analysis techniques, but the chemical information of substance with similar composition of organic polymer material cannot be obtained. So in this study, we develop electrospray dialysis (ESD) method for solving these problems. This method sprays fine droplets of nanometer order. Therefore, the selectively dissolving of target composition is possible without both transformation and changing position of sample. We confirm that this method can be selectively dissolved without breaking sample with phase separation structure like polymer alloy. And, we perform comparison between ESD method and other dissolved method and examining the influence of droplets sizes.

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## I. Introduction

Recently, materials and products development by advance technology needs for the construction of nano order. Accordingly, analysis development is desired for evaluation of structure. Among them, industrial products are necessary to identify chemical state of compound and molecular composition in micro structure. XPS is often used there. But, it is difficult to perform chemical imaging in several nanometers order. And, focused ion beam time-of-flight secondary ion mass spectrometer ([1]FIB-TOF-SIMS) is a candidate of method for imaging components at several nanometers order. But, analysis with TOF-SIMS only is difficult to perform chemical imaging. And, it is difficult to identify chemical state of compound and molecular composition in micro structure.

In this study, we developed "electrospray dialysis" method. This method is combing electrospray and FIB-TOF-SIMS which has a high lateral resolution. Thereby, we aimed to obtain component imaging of reaction process in nano order.

[2]Electrospray dialysis method can make droplets as small as a few nanometers. Therefore, it can dissolve sample in small range. And, we have developed a high resolution imaging method by using Ga Focused Ion Beam Time-of-Flight Secondary

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Ion Mass Spectrometry (FIB-TOF-SIMS). Generally, SIMS use phenomenon called sputtering when surface atoms of the sample eject into vacuum by irradiating the ion beam in vacuum. Then, a part of the sputtered atoms is ionized, called secondary ions. And, it is measured by separating it by a mass spectrometer. Thereby, analysis method is identification and concentration measurement of elements or compounds in a sample.

This method can be selectivity dissolved particles by combing two apparatus. The figure is SEM image before and after ESD of sea-salt and black-carbon (BC). In this way, it can be selectivity dissolved by electrospray dialysis method. And, like a yellow circle can be dissolved without changing the geometric arrangement. But, it has not been confirmed that dialysis can be performed without destroying shell structure and phase separation structure used in polymers, etc. And, we verify the principle of ESD method which comparing ESD method and other dissolution methods.

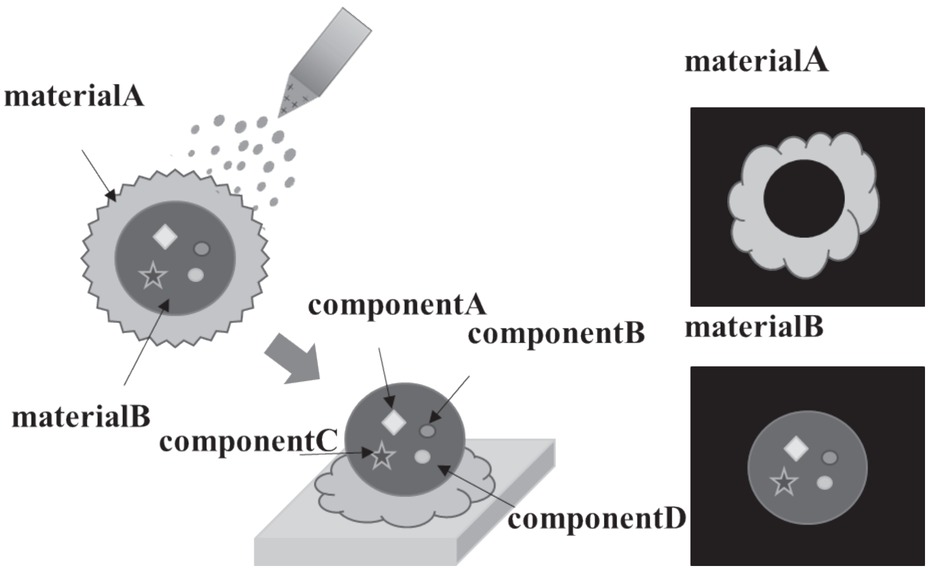


Fig. 1 Schematic diagram of electrospray dialysis

## II. Experimental

First, the powder of only tris aluminum ($Alq_3$) on a Si substrate (Nilaco, thickness: 0.5 mm, length and width: 20 × 20 mm) was used for FIB-TOF-SIMS analysis. Next, the mixed powder of $Alq_3$, aluminum (Al) and carbon (C) fixed on Si substrate was dialyzed by ESD with tetrahydrofuran (THF). Only $Alq_3$ was dissolved under this condition. The condition of ESD method is follows: distance between capillary and substrate: 40 mm, applied voltage: 3.9 kV, flow rate: 700 μL/h, spray time: 40 sec. Next, before and after dialysis component images were obtained by TOF-SIMS. And, the principle of indirect chemical imaging using ESD was verified by comparison before and after dialysis.

Next, both polystyrene (PS) and polyhydroxystyrene (PHS) dissolved in ethyl acetate was formed as sea-island structure on a Si substrate. In order to compare ESD method, the sample was immersed in the same solution, and structural change and droplets size were confirmed. The thin film samples of polymers were prepared by the following conditions. Samples were formed on a flat Si substrate by spin-coater. Solutions are PS (0.0130 g) and PHS (0.0257 g) dissolved in ethyl acetate (4.0 mL). It is stirred at a temperature of 20℃. The condition of the stirrer was 800 rpm for 24 hours. The sample drip a few drops of this solution, and its thin film was formed by spin coater (speed: 275 rpm, rotation time: 20 s). Next, it was dried by heater (temperature: 100℃, time: 10 min). Thereafter, dialysis is performed under the following condition: distance between capillary and substrate: 40 mm, applied voltage: 3.9 kV, flow rate: 200 μL/h, spray time: 60 s. Thereafter, the sea-island structure of blend polymer before and after dialysis were observed by optical microscope. Similarly, the sample was immersed in a 2-propanol for 30 s. Next, the sample was dried by heater. Thereafter, the samples before and after immersion were observed by optical microscope.

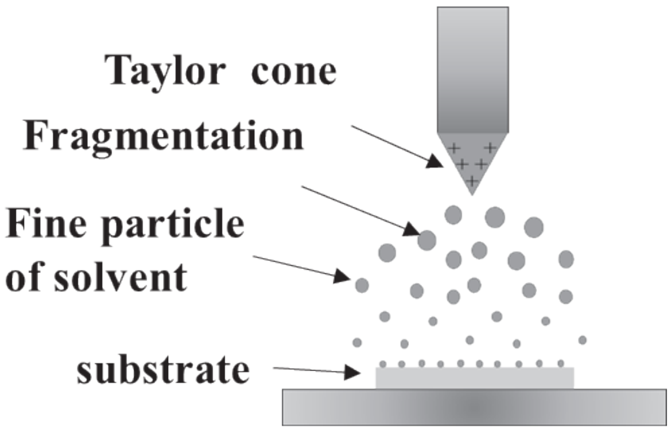


Fig. 2 Dissolution by ESD method

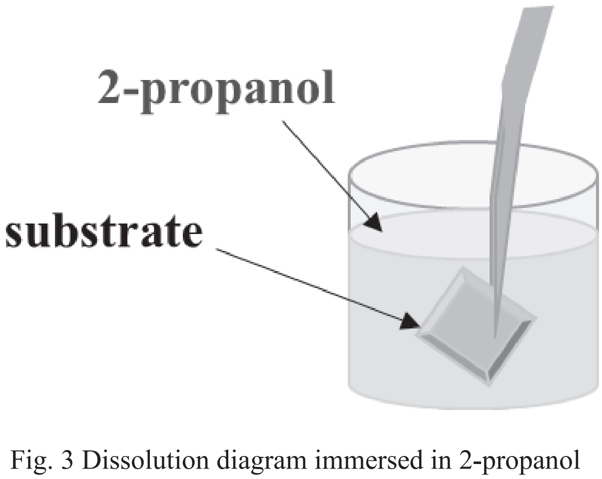


Fig. 3 Dissolution diagram immersed in 2-propanol

## III. Result and Discussion

First, component distribution of only $Alq_3$ can be seen from Fig. 4. Aluminum secondary ions were easily detected when $Alq_3$ is analyzed by TOF-SIMS. Both C and $C_2$ are detected as fragments of organic matter. On the other hand, $C_3$ and $C_4$ are hardly detected in organic matter. This can be confirmed in Fig. 4, because $Alq_3$ is organic matter. The following can be seen from the yellowish green circles in the Fig. 4 and Fig. 5. Aluminum distribution has not changed before and after dialysis. $C_3$ was hardly detected to organic carbon and, C and $C_2$ are detected. Therefore, it can be specified to $Alq_3$. And, the following can be seen from the blue circles in the Fig. 5 and Fig. 6. Al isn't detected and, $C_3$ is detected from inorganic carbon with high sensitivity. According to our experience, it can be specified to be graphite. Finally, the following can be seen from the yellow circles in the Fig. 5 and Fig. 6. C isn't detected, and Al is detected unchanged before and after dialysis. Therefore, it can be specified to Al. Therefore, it can be dissolved $Alq_3$ by THF without changing the geometric arrangement from experimental result of fig.4 to Fig. 6. And, indirect chemical imaging could be confirmed by comparison of component imaging before and after dialysis.

Next, the advantage of ESD method compared with the other dissolving technique like immersion method is discussed. Figure 7 and 8 show the optical microscopic images of sea-island structure before and after ESD with same field-of-view, respectively. The following can be seen from the red circles in the Fig. 14. It can be confirmed that part of the structure of PS is flowing. Also, compare Fig. 11 and Fig. 12. Therefore, in the case of immersing in solvent part of the structure of PS was greatly destroyed. Therefore, it can be dissolved without changing the geometric arrangement against micro area. And, ESD method thought that it was superior to other dissolve methods. Also, the following can be seen from the Fig. 14. The cause of breaking the structure of PS is considered to be that it is greatly affected comparing to ESD method by the surface tension of the liquid and free vibration.

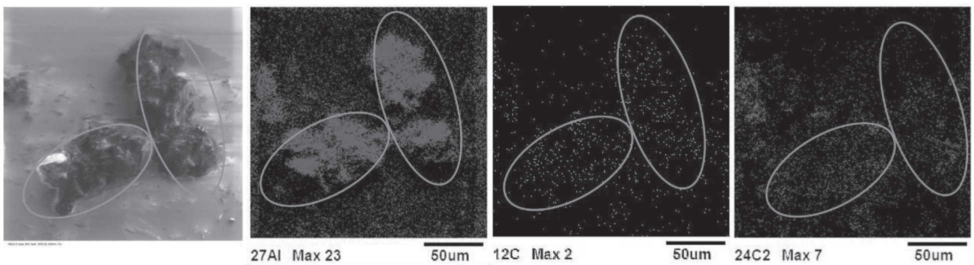


Fig. 4 : Pure $Alq_3$ powder mapping result.

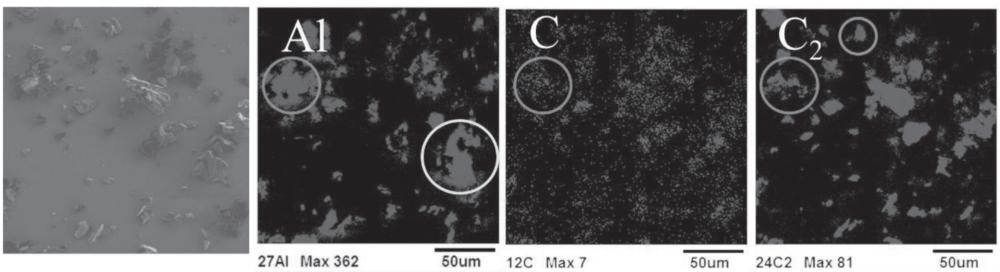


Fig. 5 Mapping before dialysis of mixed powders of $Alq_3$ and Al, C.

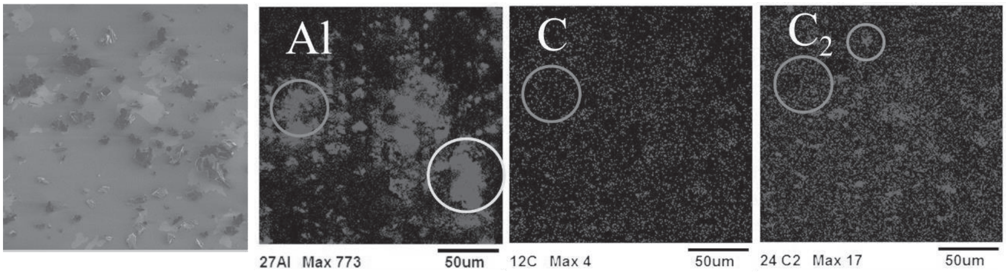


Fig. 6 Mapping after dialysis of $Alq_3$ and Al, C

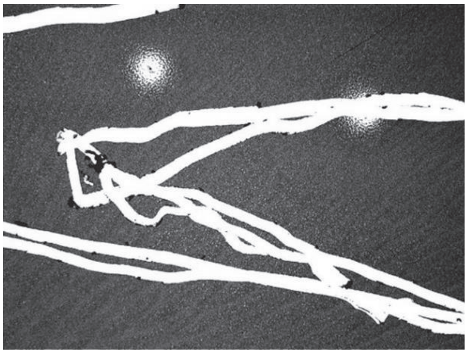

Fig. 7 Before ESD method dialysis(50x)

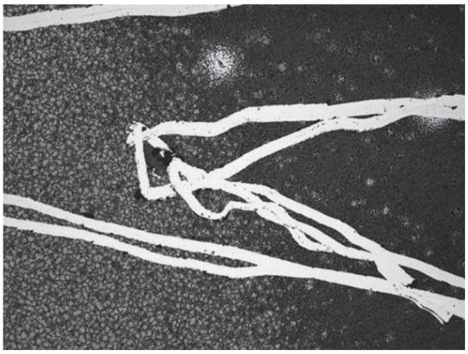

Fig. 8 After ESD method dialysis(50x)

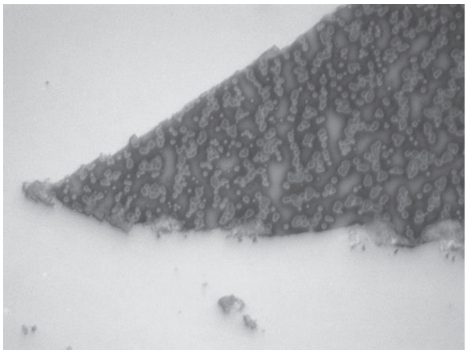

Fig. 9 Before ESD method dialysis(x1000)

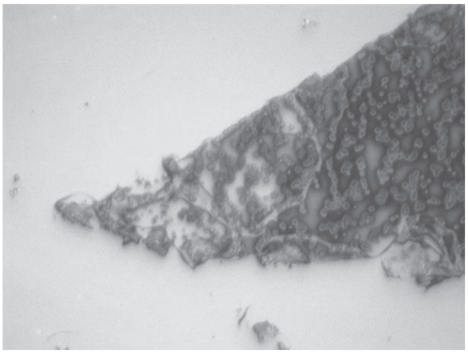

Fig. 10 After ESD method dialysis(x1000)

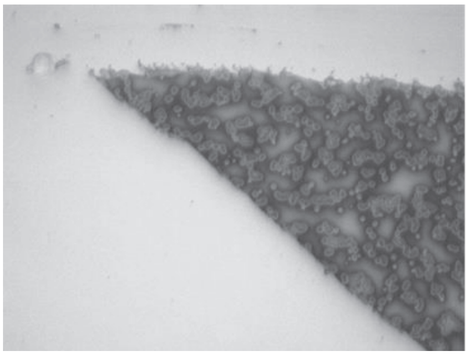

Fig. 11 Before immersion in solvent(50x)

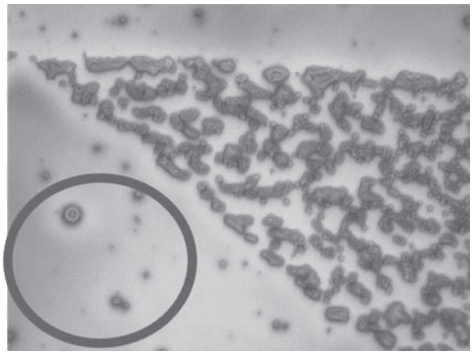

Fig. 12 After immersion in solvent(50x)

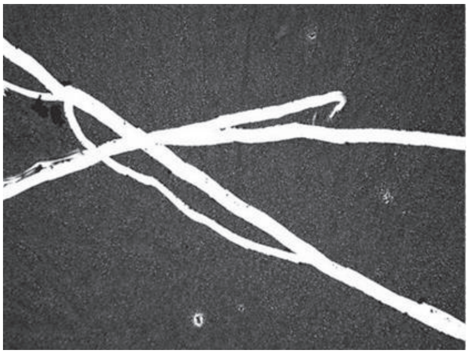

Fig. 13 Before immersion in solvent(1000x)

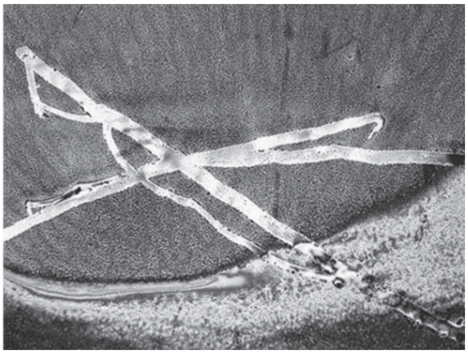

Fig. 14 After immersion in solvent(1000x)

## Ⅳ. Conclusion

In a dialysis experiment using $Alq_3$, Al, and C, the target substance, $Alq_3$, could be selected and dissolved. Further, in a dialysis experiment on a sea-island structure using a solution of PS and PHS dissolved in ethyl acetate, the target substance could be selectively dissolved without destroying the phase separation structure. Also, it can be said that the ESD method has an advantage in dissolving a target substance in a minute area as compared with a case where the substance is immersed in a solvent as it is. In the future, application of polymer-based real materials to chemical imaging can be expected.

## References

1) K. Hiraoka, *J. Mass Spectrom. Soc. Jpn.*, **58**, 139 (2010).

2) T. Sakamoto *et al., Appl. Surf. Sci.*, **255**, 1617 (2008).