Depth Profiling Analysis of Organic Materials by Using ToF-SIMS and Gradient Shaving Preparation

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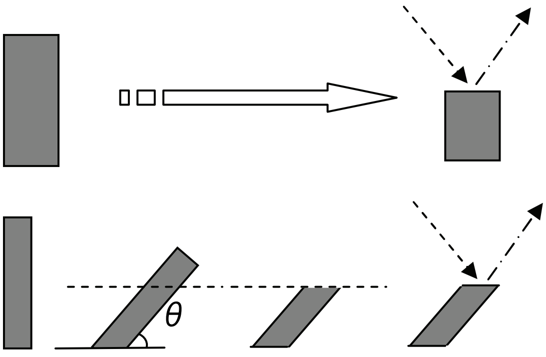
Several oblique cutting methods, including a recently developed gradient shaving preparation, for sample pretreatments have been developed. The combination of the above pretreatment method and time-of-flight secondary ion mass spectrometry provides very useful depth-profiling information in the analysis of organic materials for practical use. In this report, some results measured by combinations of the several oblique cutting methods and ToF-SIMS measurements are introduced.

1. Introduction

Static secondary-ion mass spectrometry method combined with time-of-flight mass spectrometers (ToF-SIMS), which has been widely used in recent years, exhibits excellent features, such as high surface susceptibility, moderate spatial resolution, and high detection sensitivity, compared with X-ray photoelectron spectroscopy (XPS) conventionally used for the analysis of organic materials. Since information of chemical structures existing in the very near surface of materials can be provided by analyzing peaks which appear especially in mass spectra, the ToF-SIMS is a very useful tool for analyzing surface of organic materials. In addition, as for depth-profiling analysis of organic materials, ion sputtering process using low-damage cluster ions represented by C60 has been getting popular [1-3].

On the other hand, many organic functional materials have a very variety of thickness; for example, several tens to one hundred micrometers in the case of polymer films, several tens to several hundred nanometers in the case of organic light emitting diodes (OLEDs), which have been actively developed in recent years, and several nanometers in the case of a lubricant layer on the surface of hard disks and self-organizing films. Thus, in many cases, conventional depth profiling analysis using ion etching (sputtering process) cannot be adopted for relatively thick organic materials, such as OLEDs. One effective method in the above case is composed of steps of mechanically obliquely cutting an area for analysis, preparing a measuring surface plane, and performing the ToF-SIMS measurement, similarly to a method in which a profile measurement had been carried out using so-called crater-edge method in Auger electron spectroscopy [4].

The present presentation describes some examples of depth-profiling analysis of organic materials having different coating thicknesses, which can be performed with the combination of the ToF-SIMS measurement and a pretreatment method using oblique cutting techniques, including a recently developed gradient shaving preparation.



$Mag = 1/\sin\theta$

Fig. 1 Sample preparation of a cross sectional sample by using a microtome.

2. Sample Preparation methods

2.1 Preparation of a cross-sectional sample by using a microtome

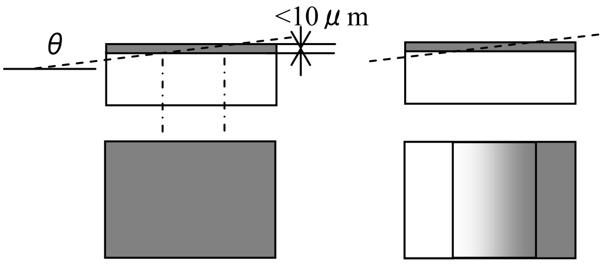
In the case of relatively thick materials, such as polymer films, a cross sectional sample can be easily obtained by using a microtome, which is usually employed for sample preparation for scanning electron microscopic observation. These samples can be provided for depth analysis of the cross sectional area.

In case of a sample of about 10 micrometers in thickness, by obliquely cutting the sample using an angular mounted knife on the microtome, the measurement area of the sample can be extended to allow analysis with higher accuracy. Figure 1 illustrates a preparation of a cross sectional sample by using a microtome.

2.2 Preparation of oblique cutting samples by using an ultramicrotome

Although the thickness of the target sample is about several 10 - 100 micrometers as described in paragraph 2.1, sufficient information on the area of, for example, several microns depth near the surface of a film, cannot be obtained from the cross-sectional preparation method in many cases. In that case, the "oblique cutting method" using an ultramicrotome is useful.

The ultramicrotome, which is primarily used for preparing a very thin sample for transmission electron microscopes, provides a sufficient extended area for an analytical measurement using the ToF-SIMS by performing an oblique cutting, using a good-quality glass knife, with an angle of several degrees between cutting surface of a sample and a glass knife. Figure 2 illustrates the sample preparation of oblique cutting samples by using an ultramicrotome.

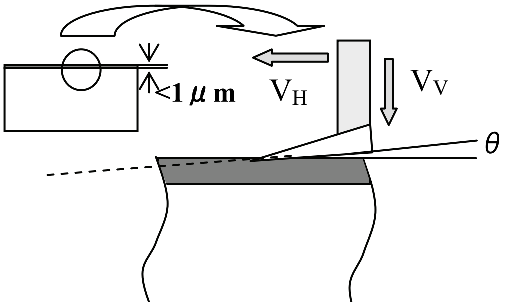


$$Mag = 1/\sin\theta$$

Fig. 2 Preparation of an oblique cutting sample by using an ultramicrotome.

2.3 Gradient shaving sample preparation using a specialized system (a gradient shaving instrument)

In using an ultramicrotome, adjusting the knife to a very shallow angle, e.g. less than one degree, with sufficient reproducibility, is very difficult, because it requires procedures of ensuring parallel between the knife and a sample surface using the shadow of the knife, and manual adjusting of the angle between the knife and the sample surface. For example, when the thickness of a sample is about several 100 nm; e.g. OLED, the oblique cutting by the ultramicrotome will become substantially impossible. In order to solve these problems, a system, ordinarily evaluating adherence of thin films (i.e. measurement of shear strength and peel off strength), has been converted to oblique cutting (which should rather be called gradient shaving) preparation since several years. It is possible to shave off, at a very shallow angle, sample surface by precisely driving the knife made of diamonds by a piezoelectric device, and using a driving speed difference between horizontal and perpendicular directions, thereby shaving can be achieved at very shallow angle with respect to sample surface, that is, the order of less than 0.1 degree, and typically 0.02 degrees [5-7]. Figure 3 illustrates the sample preparation using a specialized system (a gradient shaving instrument).

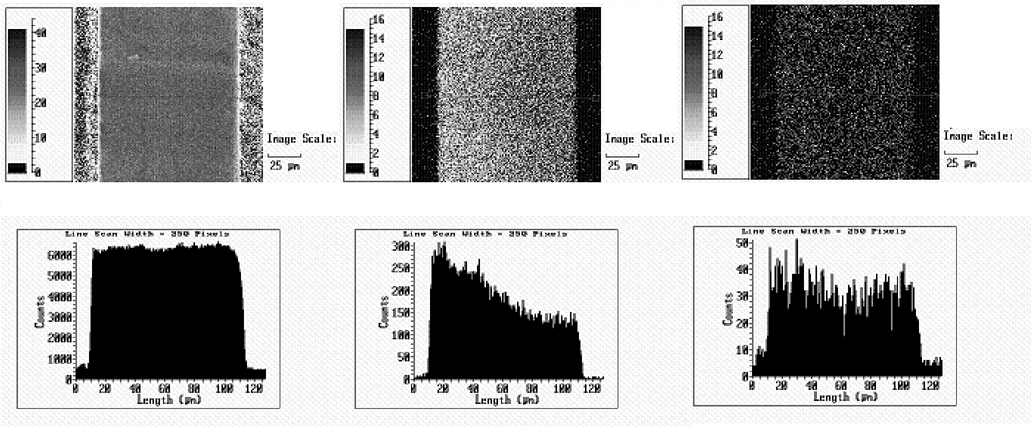


$$Mag = V_H / V_V \cong 1/\sin\theta$$

Fig. 3 Gradient shaving sample preparation using a specialized system (a gradient shaving instrument).

3. Examples of the measurement

The examples of the measurements using each method mentioned above are shown below. In all ToF-SIMS measurements (Physical Electronics, model 2100TRIFT2), an In^+, as a primary ion, was mainly used. DuPont SORVALL MT6000 was used to prepare oblique cutting samples. DAIPLA WINTES SAICAS model NN04 was used to prepare precise gradient shaving samples.



A）Substrate B）Additive 1 C）Additive 2

Fig. 4 Cross-section Ion image of film.

3.1 Cross-sectional measurement of the film

Figure 4 shows results of the ToF-SIMS of a cross sectional film sample prepared by a solution cast method. Two kinds of additives are incorporated into the film. The figures A), B), and C) show an ion image of the film substrate, an ion image of additive 1, and an ion image of additive 2, respectively. Different distributions can be seen in the depth direction with respect to additive species.

3.2 Depth profiling analysis near the slanted cut film surface by using the ultramicrotome

Obliquely cut surface of a functional film using the ultramicrotome is shown in Figure 5, in which the film surface was coated to a thickness of two micrometers, and their ion images obtained by the TOF-SIMS measurements are also shown in Figure 5. The figures A), and B) show an optical microscope image of a sample, and a line scan of signal intensity from an additive, respectively. The line scan of an additive shows that the additive also spread into the coating layer. It is well known that diffusion of additives may affect mechanical properties such as hardness of surface coating layer and adhesive properties.

3.3 Depth profiling analysis of a film by using a precision gradient shaving instrument

The paragraph 3.2 describes the functional film coated with a material in several micrometers thick, and it is possible to prepare an oblique cutting surface using the ultramicrotome. On the other hand, it is not easy to prepare an oblique cutting surface of a film coated to a thickness of less than one micrometer on, for example, a glass substrate. In this case, a precision gradient shaving instrument may be effective.

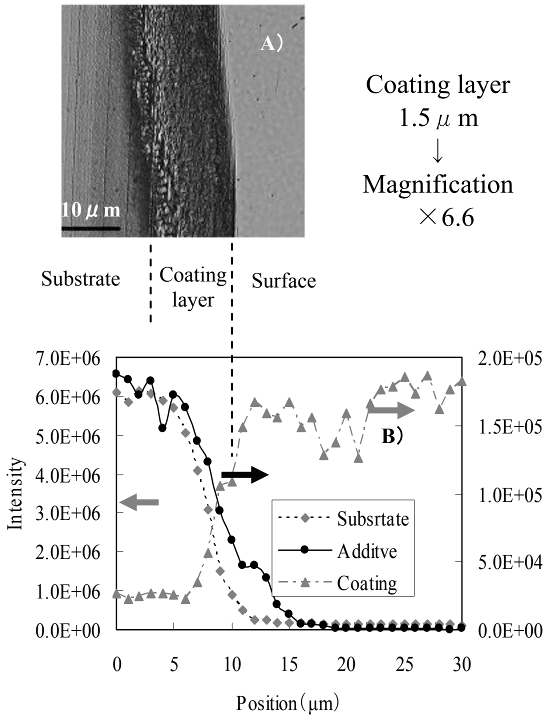


Fig. 5 Depth profiling analysis near the slanted cut film surface.

A） Optical image of Sample

B） Line scan of ion signal intensity

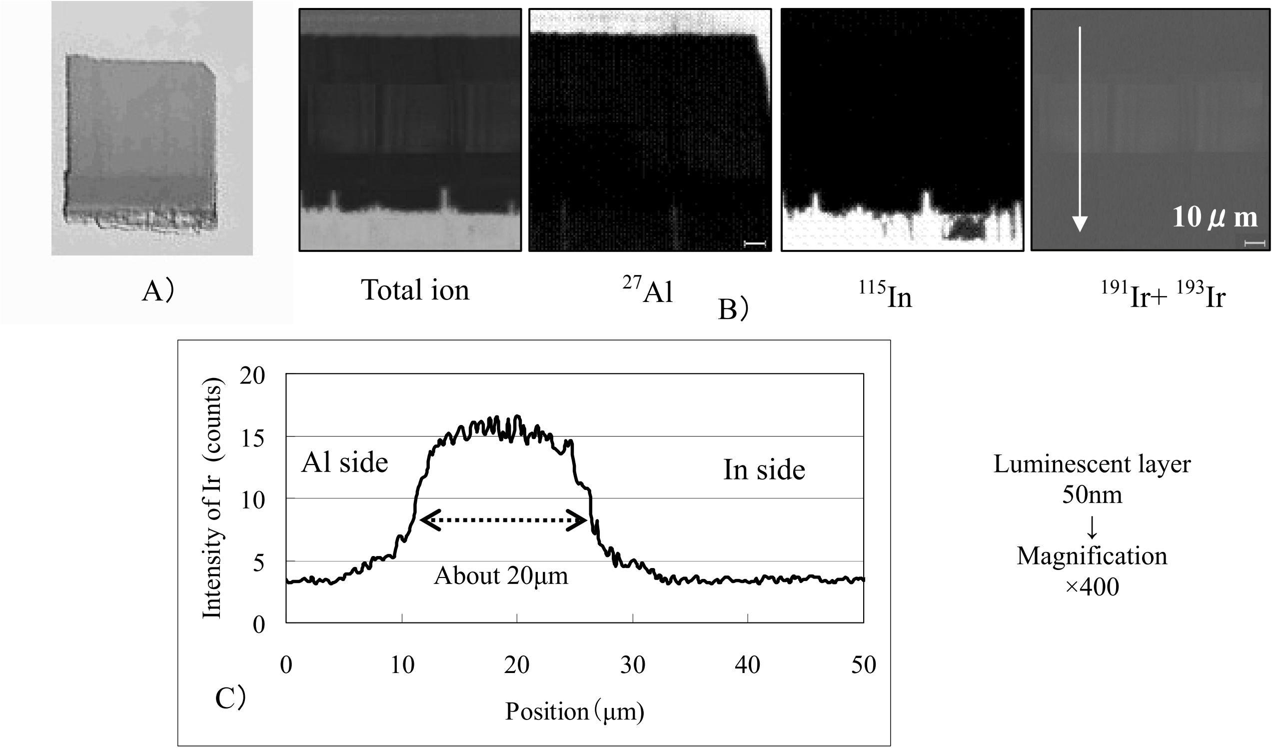


Fig. 6 Depth profiling analysis of OLED using the precision gradient shaving instrument.
A) Optical image of sample
B) Ion image
C) Line scan of iridium ion signal intensity

Gradient shaving surface images of laminated films of OLED (Thickness is about 200 nm), and their ion images obtained by the ToF-SIMS measurement are shown in Figure 6. Iridium ions are detected near the middle layer of the laminated film, indicating that the location of a luminescent layer can be identified.

4. Conclusion

Excellent quality data can be provided by a combination of the ToF-SIMS measurement and the oblique cutting methods, including a gradient shaving preparation, in a relatively short period of time without any damages, by choosing appropriate preparation methods corresponding to the thickness of targeted materials. Application of the present preparation methods is difficult to materials of several nanometers in thickness which are generally used for surface analysis, but, for preparation of practical materials of several tens of nanometers or larger in thickness, the methods are very useful. When a depth profiling analysis by ion etching will become popular in the future, more detailed information can be obtained in a combination with the gradient shaving preparation.

5. References

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