Determination of Chemical Composition in Multilayers Polymer Film using ToF-SIMS

Journal:	*Analytical Methods*
Manuscript ID	AY-ART-02-2018-000344.R1
Article Type:	Paper
Date Submitted by the Author:	06-Apr-2018
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Running title: ToF-SIMS Analysis of Multilayer Film

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Time-of-flight secondary ion mass spectrometry is a widely used surface analytical technique, which can provide chemical information from both the uppermost surface and underneath the surface for various materials. For identification of the structure of a multilayer polymer film with unknown chemical composition, it is generally not practical to perform depth profiling using atomic ion sputtering because it will destroy the chemical information and it is difficult to obtain accurate chemical depth distributions. In this study, we present an alternative approach to microtome the polymer film to reveal the multilayer cross section followed by imaging the cross-section with bismuth liquid

metal ion gun (LMIG). To identify the spatial distribution of the thin inorganic layer in the multilayers film, bismuth sputtering was employed on the same analysis area to remove organic mass interference. Overlaid images from two separate analyses allow us to determine both inorganic and organic layers chemically and laterally with high lateral resolution.

I. INTRODUCTION

Multilayer laminate film consists of both polymeric and inorganic layers that are widely used in a variety of industries.[1-5] They can be found in adhesives, various packaging, coatings and many others.[6-7] Through lamination manufacturing, the multiple layer composite material achieves improved strength, stability, sound insulation, appearance or other properties to be used for different applications. For example, in food packaging, laminates are used not only as a functional barrier to protect the food and isolate it from the outer environment, but also to retain its aroma and flavors, and to extend the shelf life.

To both polymer film manufacturers and end users, it is important that the quality and chemical composition of the polymer films meet specification. For example, the layer thickness measurement, polymer identification of each layer and metal composition are typical information of interest to manufacturers. In addition, it is important to identify any defects and/or inclusions in the polymer. When foreign particles get into the polymer during manufacturing, they form inclusions in the final product, which will shorten the shelf life. It is important both to the manufacturers of the films as well as to the final industries using these films that the quality and composition be strictly controlled and monitored.

However, the multiple layer nature with some very thin layers and the diversity of the material chemistry involved from both organics to inorganics present significant analytical challenges. Traditional analytical methods have certain drawbacks. For example, a bulk technique such as NMR doesn't have the spatial resolution for in-situ analysis, and is not suitable for inorganics. Imaging microscopic techniques have the spatial resolution but lack chemical information.[8] Raman and IR imaging have a limitation on the thickness of the film (under 1 μm) and are not effective on inorganic layers.[9-10] Todate, there are not many available analytical techniques to identify the chemical composition, defects and inclusions on polymer films without extraction. The confocal analysis and high spatial resolution of Raman microscopy have been employed.[10] However, the spatial resolution of Confocal Raman is on the order of one micrometer, which can not meet the analysis requirement.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been proven to be a valuable and powerful analytical technique in surface analysis due to its ability to determine chemical composition with high spatial resolution at several hundred nanometers and high elemental sensitivity.[11-13] In recent years, SIMS has been widely used for chemical characterization of concentration profiles in multilayered organic materials. Cluster ion sources such as C_{60}^{+} and more recently gas cluster ion beams (GCIB) have advantages over atomic ion beams for organic depth profiling because of reduced beam-induced damage caused during the sputtering process.[14-16] However, organic depth profiling and depth resolution can be affected by many factors, such as initial surface roughness, ion-induced roughening, differential sputtering of the various elements, primary ion beam implantation induced ion mixing, etc. Moreover, the ability to obtain organic depth profiles is restricted by the availability of cluster ion sources. The time consumed to analyze more than 100 μm film thickness is relatively long. Alternatively, high lateral resolution ToF SIMS imaging can be performed on a well-prepared multilayer film cross section. This will not only reveal the chemical composition, but also provide good lateral resolution of the multilayer film within a short period of time.

In this paper, we present the use of TOF-SIMS as an ideal tool for multiple layer film analysis which provides sufficient spatial resolution on even *sub*-μm layers and rich chemistry information on both organic (polymeric) and inorganic layers.

II. EXPERIMENTAL

An industrial multilayer film with limited chemical information was used in this study. The film was sandwiched between two pieces of polystyrene with cyanoacrylate adhesive. The cross section was prepared using Leica® EM UC7 (Leica, Buffalo Grove, IL) with cryo-attachment at a temperature of -40ºC using a 45º cryo-diamond knife. The cryo-temperatures were necessary to avoid smearing of both the fiber surface and the embedding media and prevent distortion or contamination of the fibers. The temperature of -40 °C proved to be optimum producing sections with minimal curling and no apparent smearing of the surface. A thickness of 500-700 nm proved to be sufficient to immobilize the film and prevent pull-out. Sections were excised from the diamond knife with an eyelash brush and placed onto a drop of water on a clean single crystal Si wafer. The surface tension of the water stretches the sections to flatten them as the water droplet evaporates. The water was allowed to evaporate and the sections were stored in Fluoroware® containers to prevent surface contamination until they were analyzed.

ToF-SIMS analyses were performed using a ION TOF ToF SIMS V instrument. The instrument is equipped with a Bi_n^{m+} (n = 1 - 5, m = 1, 2) liquid metal ion gun, Cs^+ sputtering gun and electron flood gun for charge compensation. Both bismuth and cesium ion columns are oriented at 45° with respect to the sample surface normal. The analysis chamber pressure is maintained below 5.0×10^{-9} mbar to avoid contamination of the surfaces to be analyzed. For high mass resolution spectra acquired in this study, a pulsed Bi_3^+ primary ion beam at 25 keV impact energy with less than 1 ns pulse width was used. An electron gun was used for charge neutralization. The mass resolution on a silicon wafer is ~8000 m/Δm at 29 AMU. For high lateral resolution mass spectral images acquired in this study, a Burst Alignment setting of 25 keV Bi_3^+ ion beam was used to raster a 100 µm by 100 µm area. The spatial resolution of the image acquired under this setting is around 300 nm. The negative secondary ion mass spectra obtained were calibrated using C^-, O^-, OH^-, C_n^-, respectively. The positive secondary ion mass spectra were calibrated using C^+, $C_2H_3^+$, $C_3H_5^+$, and $C_4H_7^+$.

III. RESULTS AND DISCUSSION

To reveal the multilayer structure and their chemical composition, ToF SIMS analysis was performed on a prepared cross section area. Since the multilayer film is thin and soft, it requires identification of a material with mechanical properties similar to the film as the embedding media. The common Eponate™ 12 (Ted Pella) was used initially with little success in various hardness formulations. Instead of embedding, the problem was solved by sandwiching the films between two pieces of polystyrene with a cyanoacrylate adhesive. Cyanoacrylate adhesive is a fairly novel media for embedding samples for analysis by high vacuum characterization equipment. The adhesive is ideal in that it does not outgas in high vacuum. It can withstand high current analysis beams of TEM or ToF SIMS and it has low viscosity, high adhesion and sections readily in the ultramicrotome. In cases where a sample does not section well or has physical limitations that will not allow microtoming, it can be sandwiched between two pieces of a material that do section well, such as polystyrene, and glued with the cyanoacrylate. The polystyrene helps guide the knife and allows sectioning.

The structure was squeezed together with a binder clip to apply pressure while the adhesive cured. After curing overnight, the binder clip was removed and the sandwiched structure was trimmed and a mesa formed as typical in microtome preparation. Figure 1 shows pictures of the multilayer thin film (1a), the sandwiched structure with a binder clip (1b) and the optical image of the cross section (1c). Note that the optical image was captured with the microscope camera attached to the ToF-SIMS instrument. Polystyrene parts were detached during microtoming or transferring.

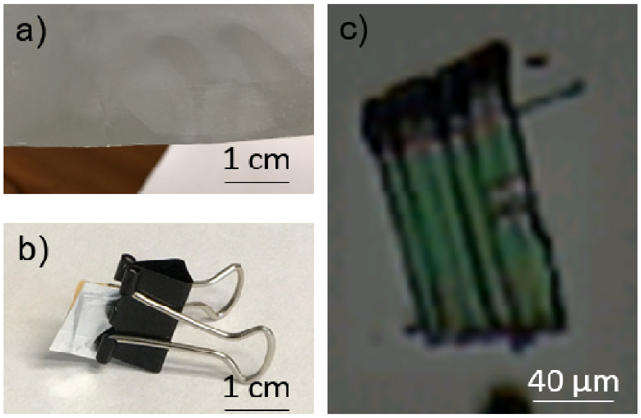

FIG. 1. (color online) a) Picture of multilayer polymer film used in this study. The shinny finish of the film indicates metal layers. The thickness of the thin film is below 100 µm. b) Curing the sandwiched thin film with binder clip. Two pieces of multilayer film were glued with Cyanoacrylate adhesive followed by sandwiching between two pieces of polystyrene with thickness on the order of 1 mm. c) Optical image of the multilayer film cross section.

High current bunched mode was first applied to acquire high mass resolution spectra on the multilayer cross section. The exact masses obtained were used to assign the chemical formula of the fragment ions and to determine the chemical composition of the polymers. High spatial resolution images, in many cases, could be originated from several ions with the same unit mass. Therefore, mass interferences needed to be identified using high mass resolution spectra.

Figure 2 shows both positive and negative ion mass spectra obtained from a multilayer polymer film cross section. Several characteristic ions of polyethylene terephthalate (PET) were identified including $C_7H_4O^+$ (*m/z* 104), $C_9H_9O_2^+$ (*m/z* 149), $C_7H_4O_2^-$ (*m/z* 120) and $C_7H_5O_2^-$ (*m/z* 121).[17] When acquiring high spatial resolution mass spectral images, these PET fragments were then chosen to illustrate the layout of the film structure. Besides these characteristic PET fragments, a few other ion fragments attributed to polydimethyl siloxane PDMS and fatty acids were observed. The peak identifications are labeled in Figure 2. One PDMS characteristic peak in positive ion mode is $SiC_6H_{15}O_2^+$ at *m/z* 147. Ions observed at *m/z* 241 and 255 are assigned to $C_{15}H_{29}O_2^-$ and $C_{16}H_{31}O_2^-$, which are characteristic ions of fatty acid.

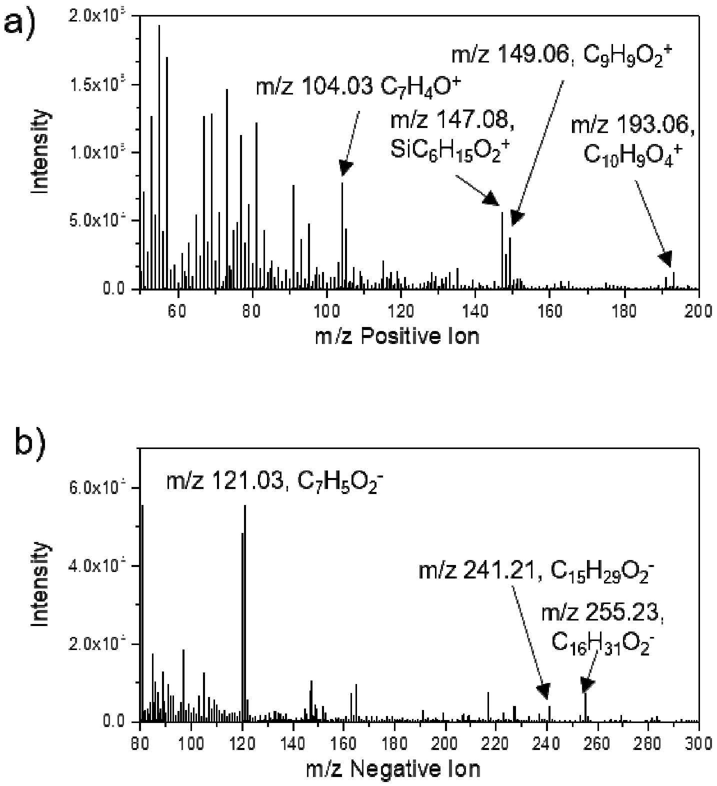

FIG. 2. a) Positive ion and b) negative ion mass spectra obtained from multilayer polymer film cross section area. The high mass resolution spectra show characteristic ions of polyethylene terephthalate (PET) and ions from PDMS and fatty acid contamination.

From the high mass resolution spectrum, composition of the main polymer film was identified to be PET. The following task was to determine chemical composition of lamination layers. Since limited chemical information was available for the film, an initial trial was to choose ions showing relatively higher intensity in the spectrum. In addition to $C_7H_4O^+$ at *m/z* 104, $C_4H_7^+$ at *m/z* 55 and $C_3H_8N^+$ at *m/z* 58 were selected. Figure 3 displays the individual and overlaid images of these three ions. $C_7H_4O^+$ showed predominantly high ion intensity in three thick layers, suggesting the polymer in these layers was PET. The long chain alkyl fragment showed higher ion intensity in two thinner layers, which were in between PET layers. The image of $C_3H_8N^+$ showed the location of the cyanoacrylate adhesive. The overlaid image of these three ions indicated a film structure with five polymer layers. An intensity profile line was drawn across the multilayer and showed that the thickness of PET was around 10 μm and the two thinner layers was aroun 5 μm. The negative ion image of $C_7H_5O_2^-$ at *m/z* 121 further confirmed that the polymer of the three thick layers was PET (Figure 4). The thinner layers between PET layers were most likely a type of adhesive for the purpose of lamination. From positive ion ToF SIMS spectrum and image, we knew that the lamination layer comprised a long chain alkyl group. In the negative ion image, these layers were predominately associated with CNO^- at *m/z* 42 and with an ion at *m/z* 121 (Figure 4). CNO^- is indicative of imide bond or carbamate bond. The ion at *m/z* 121 could be assigned either to $C_7H_5O_2^-$ or $C_7H_7NO^-$ as shown in Figure 5. The high lateral resolution image of *m/z* 121 displayed the spatial distribution of the combination of these two ions. The latter can originate from the rigid segment of aromatic diisocyanates from polyurethane (PU). Together with the long chain alkyl fragment $C_4H_7^+$ observed from the positive ion image, chemical composition of the adhesive was tentatively assigned to be polyurethane (Figure 6).[18] Although it was hard to define the exact chemical formula of the adhesive, ToF-SIMS analysis helped to narrow the identification of the adhesive to polyurethane.

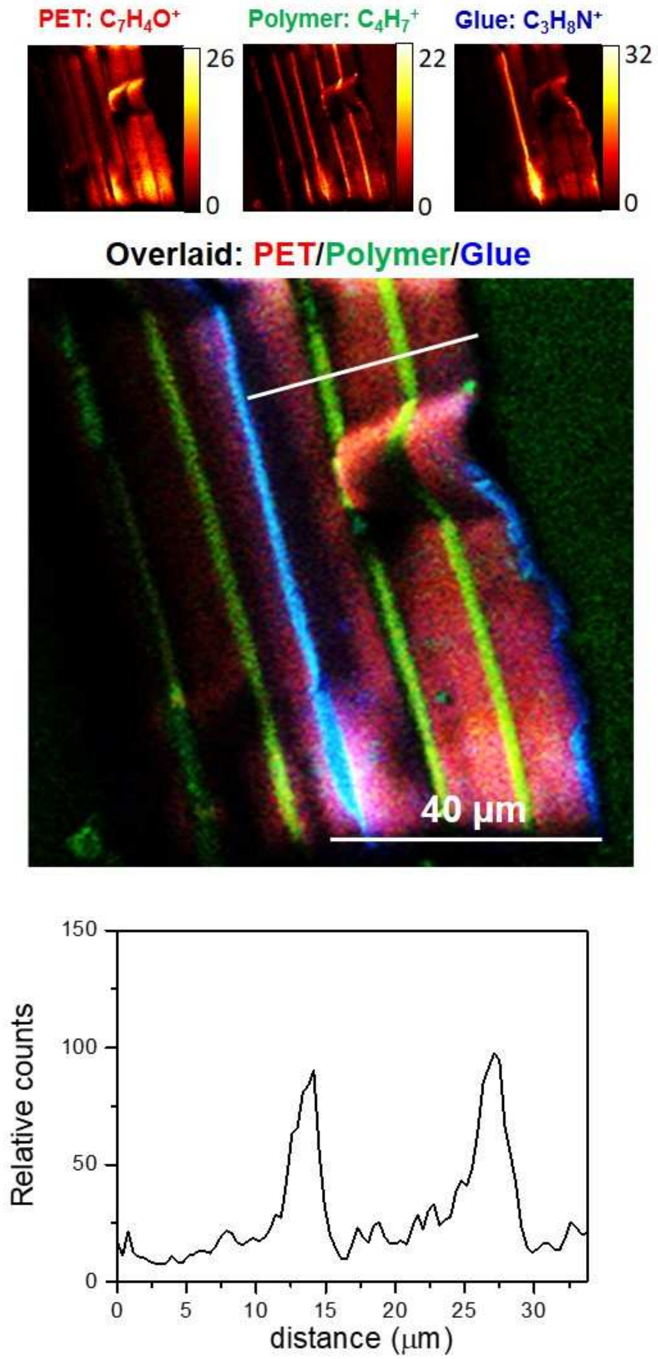

FIG. 3. (color online) Positive ion high lateral resolution images of $C_7H_4O^+$ at *m/z* 104 (in red), $C_4H_7^+$ at *m/z* 55 (in green) and $C_3H_8N^+$ at *m/z* 58 (in blue), as well as the overlaid image of these three ions. The profile line shows the thickness of each layer.

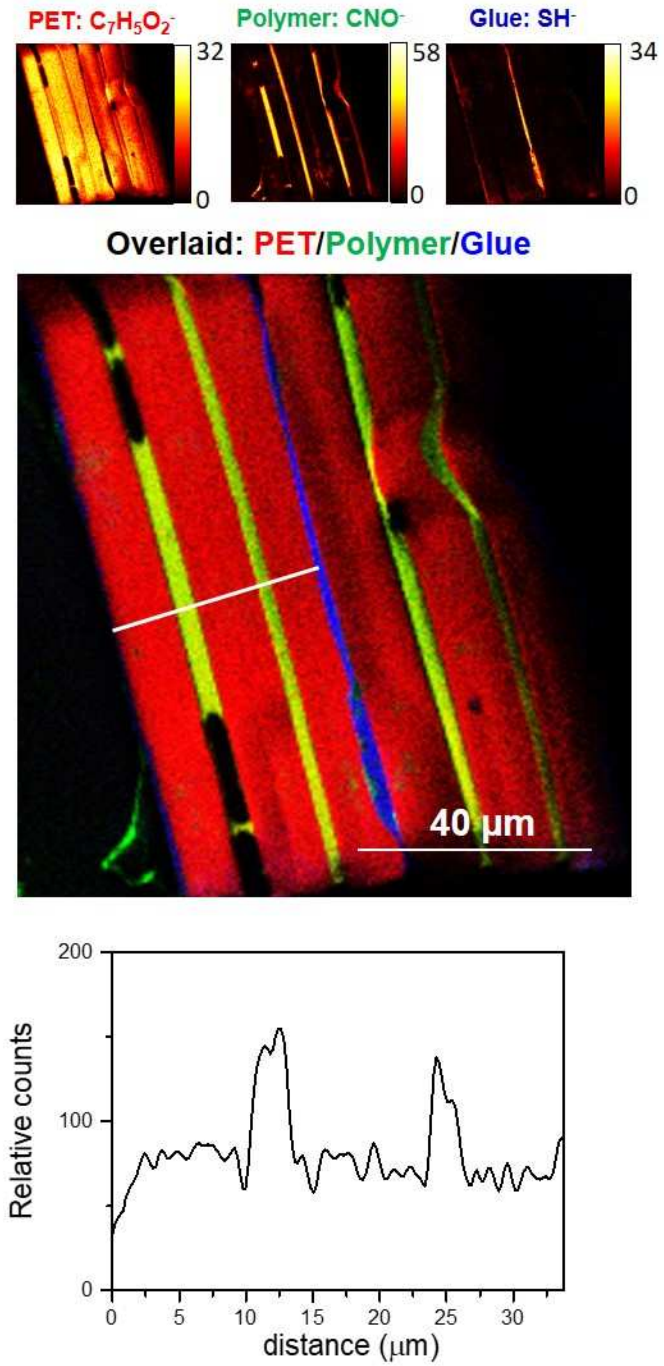

FIG. 4. (color online) Negative ion high lateral resolution images of $C_7H_5O_2^-$ at *m/z* 121 (in red), CNO^- at *m/z* 42 (in green) and SH^- at *m/z* 33 (in blue), as well as the overlaid image of these three ions. The profile line shows the thickness of each layer.

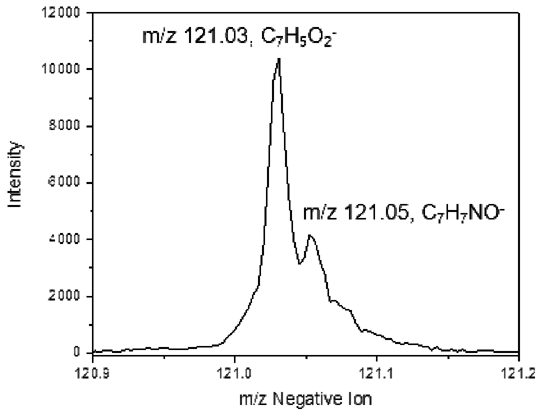

FIG. 5. Negative ion mass spectrum at m/z 121 including two ion fragments of $C_7H_5O_2^-$ and $C_7H_7NO^-$.

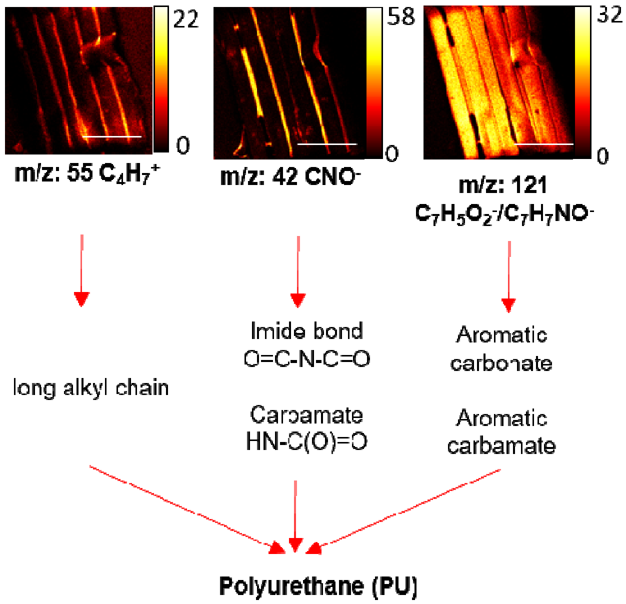

FIG. 6. (color online) High lateral resolution images of ions attributed to adhesive layers. The combination of these three ions at $C_4H_7^+$ at *m/z* 55, CNO^- at *m/z* 42, $C_7H_5O_2^-$ /$C_7H_7NO^-$ at *m/z* 121 indicated the adhesive was polyurethane (PU).

Many packaging materials, especially for high value foods, contain layers of aluminum foil as it is an effective barrier against moisture, air, odors and UV light.[19] The multilayer film analyzed in this study also contains metal layers. From the high mass resolution spectrum shown in Figure 7, Al^+ at *m/z* 27 was observed. However, the mass interference of $C_2H_3^+$ makes it difficult to map the aluminum distribution in a high lateral resolution image. The problem was solved by gently sputtering the cross section area with 25 keV bismuth direct current beam with 14 nA current. The high current ion beam was rastered over 200 μm × 200 μm with 128 pixels x 128 pixels for 5 frames, which corresponded to 8.4 seconds. The total fluence is 1.1×10^{15} ions/cm^2, which exceeds the static limit.[11] As a result, the organic chemical information was significantly reduced. After sputtering, a high mass resolution spectrum (Figure 7) was then acquired to confirm the disappearance of $C_2H_3^+$ due to high ion fluence. A a high spatial resolution image of mass 27 was then acquired to mainly show Al distribution. Figure 8 shows the overlaid image of PET in red, PU in green and aluminum in blue. It clearly showed that there were three aluminum layers. Two Al layers are on both sides of the first PU adhesive and the other layer is between the second PU adhesive and PET layer.

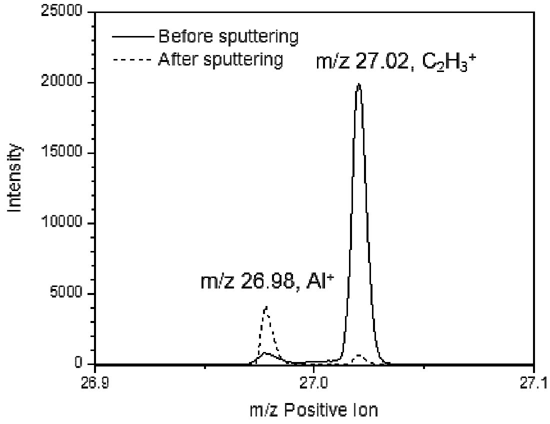

FIG. 7 Positive ion mass spectra at m/z 27 before and after bismuth direct current sputtering on the cross sectioned multilayer film area.

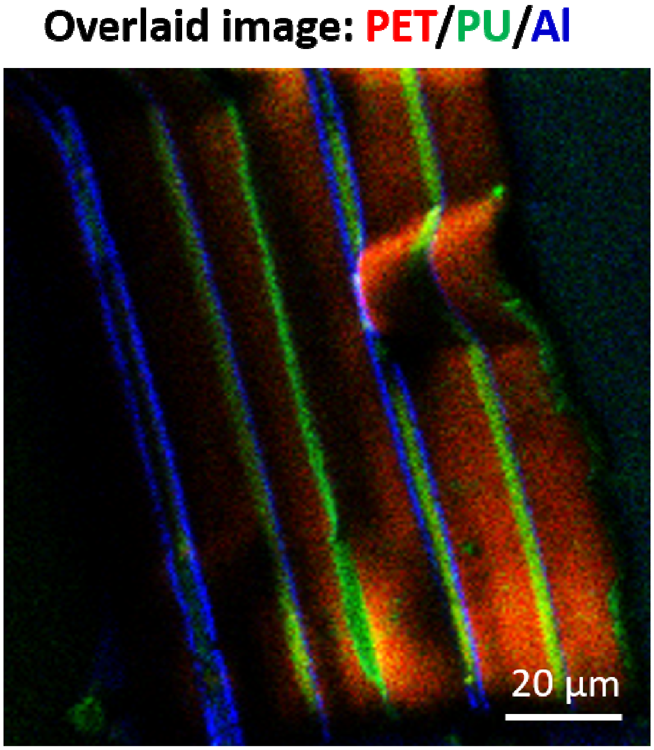

FIG.8 (color online) Overlaid image of $C_7H_4O^+$ at *m/z* 104(in red), $C_4H_7^+$ at *m/z* 55 (in green) and Al^+ at *m/z* 27 (in blue).

Figure 9 shows the multilayer diagram derived from ToF-SIMS analysis. The multilayer film contains three layers of PET and three layers of aluminum laminated with two layers of Polyurethane adhesive.

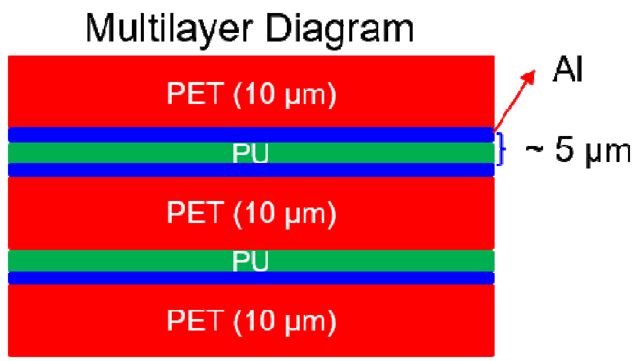

FIG. 9. Diagram of the multilayer film deduced from ToF-SIMS analysis.

IV. SUMMARY AND CONCLUSIONS

We successfully achieved full resolution of a multilayer film in both chemical composition and multiple layer construction and thickness using ToF-SIMS. The sample preparation is critical to the analysis. In this study, we have developed a new approach to microtome the polymer film to reveal the multilayer structure. Instead of curing the film with resin, it was sandwiched between two polystyrene films with Cyanoacrylate glue. The cross section was cut using a diamond knife at -40°C to avoid smearing. ToF-SIMS high mass resolution spectra and high lateral resolution images were acquired from the cross section area to reveal the organic chemical identity of different layers. To map the spatial distribution of thin metal layers, Bi^+ direct current beam was applied to sputter on the cross section to remove organic mass interference. Overlay of images from two analyses from the same area results in the determination of both organic and inorganic layer composition. The method developed in this study provides an alternative way to prepare and analyze multilayer polymer films with ToF-SIMS. We believe this method can be used to map multilayers with sub-micron spatial resolution at dramatically reduced analysis time. The spatial resolution is not comparable to wedge crater bevelling method[20], which offers sub 10 nm depth resolution. However, this method is more suitable for a thicker multilayer film.

CONFLICTS OF INTEREST

There are no conflicts to declare.

ACKNOWLEDGMENTS

This work was performed in part at the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation (award number ECCS-1542015). The AIF is a member of the North Carolina Research Triangle Nanotechnology Network (RTNN), a site in the National Nanotechnology Coordinated Infrastructure (NNCI).

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