Study on a Novel Sample Preparation Method for Organic Materials in Atom Probe Tomography*

Yutaro Hirai,[†] Yun Kim, and Tsuyoshi Yukawa
*Institute of Industrial Science, The University of Tokyo,
Komaba 4-6-1, Meguro-ku, Tokyo 153-8505, Japan*

Masanori Owari
*Institute of Industrial Science, The University of Tokyo,
Komaba 4-6-1, Meguro-ku, Tokyo 153-8505, Japan, and
Environmental Science Center, The University of Tokyo,
Hongo 7-3-1, Bunkyo-ku, Tokyo 113-0033, Japan*

(Received 8 December 2015; Accepted 17 March 2016; Published 14 May 2016)

It is important to study the distribution of host and guest molecules in organic electroluminescence materials because their distribution dramatically affects the functionalities of these materials. In order to understand this distribution, a new analysis method should be developed to obtain sub-nanometer scale information. In this regard, we used Atom Probe Tomography (APT). APT is a three-dimensional analysis technique with sub-nanometer scale resolution and is frequently used in material science and engineering. There are many reports on the analysis of inorganic materials using APT analysis, however only a few studies report the analysis of organic materials because of difficulties in the sample preparation, measurements, and the three-dimensional reconstruction of organic materials. In this study, we focused on developing a new sample preparation method and suggested the new sample preparation method for the analysis of organic materials. This new preparation method needs only a small amount of organic materials for analysis. Moreover, it is very simple and combines electrolytic polishing with the dipping method. [DOI: 10.1380/ejsnt.2016.154]

Keywords: Atom Probe Tomography; APT; Sample Preparation; Coatings; wetting; Iridium; Tungsten; Surface tension

I. INTRODUCTION

There are many organic materials in our daily life and organic semiconductors are one of these materials. Organic semiconductors are used in a variety of electronic devices (e.g. light-emitting diodes and field-effect transistors [1, 2]). The performance of such electronic devices with organic semiconductors is found to be nearly equivalent to those with inorganic semiconductors [3]. Some organic semiconductors have host and guest molecules, and understanding the distribution of these molecules is important to understand the performance of an electronic device [3, 4]. However, organic semiconductors are becoming smaller and more complex in accordance with recent developments in electronic devices; therefore, the methodology used for the analysis of these materials must also be on sub-nanometer scale resolution [5, 6]. Atomic Force Microscopy is known as an analytical method that can help determine the structures of a material surface at the atomic level [7]. Time-of-Flight Secondary Ion Mass Spectrometry, with cross-section processing of the sample, is known for affording three-dimensional information [8, 9]. However, this method does not afford three-dimensional information of a sample structure with sub-nanometer scale resolution. Atom Probe Tomography (APT) can also be used to obtain three-dimensional information of a sample. Although a large number of reports on APT focus on inorganic materials, only a few studies report on organic materials because of the associated challenges

such as difficulties in sample preparation, measurements, and three dimensional reconstruction of organic materials [10–14].

APT is a useful analytical tool for characterizing the three-dimensional structure of samples with sub-nanometer scale resolution. In APT, a needle-like tip is used in the experiment. When a high positive voltage is applied to the tip, field evaporation occurs and atoms are emitted as ions from the apex of the tip. Subsequently, the ions are accelerated by a local electrode, causing them to fly toward the detector. Elemental and three-dimensional information is then obtained using a time-of-flight mass analyzer and from the arrival position of the ions on the detector. Finally, three-dimensional images are reconstructed by using this information.

However, some problems need to be overcome before APT could be used as a feasible method for the analysis of organic materials. One problem is that tips can sometimes break under high voltages required for organic materials. This problem can be resolved to some extent by using laser assisted APT [14–16]. Although pulse voltages are not used for ionization in this method, the analyses of organic materials can be carried out. However, there are other problems with APT that disturb the analysis of organic materials, such as sample preparation methods. The dipping method is known as one of the preparation method and the studies about organic samples such as self-assembled monolayers are reported [17, 18]. Organic molecules should uniformly adhere to the apex of the carrier tip for APT. When the solution adheres to the carrier tip, the degree of adhesion depends on the affinity between the solutions and the carrier tip. Organic molecules do not always adhere to the carrier tip because of their reduced affinity for the tip. Moreover, because in the dipping method, the tip is soaked only in that solution in which molecules are dissolved, and the tip cannot

* This paper was presented at the 10th International Symposium on Atomic Level Characterizations for New Materials and Devices '15, Shimane Prefectural Convention Center (Kunibiki Messe), Matsue, Japan, October 25-30, 2015.

[†] Corresponding author: y-hirai@iis.u-tokyo.ac.jp

FIG. 1. The derivative of the Ir complex.

be made sharper. Another problem is that the carrier tip sometimes breaks under the impact of dipping. In addition, exposure to air between the electrolytic polishing and the dipping stage can contaminate the carrier tip.

The Focused Ion Beam (FIB) processing method is also used for sample preparation [19–21]. In this method, the processing of the tip is easy and a sharp tip can be obtained. However, the tip is often damaged because gallium ions are shot into the sample surface during FIB processing. Therefore, the distribution of atoms in the tip is different from the original distribution. In addition, when the targets for observation are composed of light atoms, the contamination effect becomes larger.

In this study, we propose a new sample preparation method for organic molecules that has the merits of both the dipping method and the FIB processing method. Some operations that are different from the dipping method were adopted after electrolytic polishing in the new method.

II. EXPERIMENTAL

In this study, the derivative of Tris(2-phenylpyridin-2-yl)iridium (III) (Fig. 1), a well-known electroluminescent Ir complex, was used. A tungsten wire of 0.1 mm diameter (purity = 99.95%, The Nilaco Corporation) was used as the carrier tip. A nickel ring (diameter = 0.8 cm), made from a nickel wire of 1.0 mm diameter (purity = 99%, The Nilaco Corporation), was used in the electrolytic polishing equipment. Electrolytic polishing was conducted by passing a tungsten wire through the nickel ring, followed by passing an electrical current through the system. A nickel wire was used as the electrode and 5% NaOH_(aq) was used as the electrolyte solution. A potential of 4.4 V was applied to the electrode for the first 5 s. Then, the potential was reduced to 3.8 V and was maintained constant until the completion of electrolytic polishing. Subsequently, the dipping method was then performed by soaking the tip into the solution to compare its results with those of the new method.

In our new method, electrolytic polishing was performed at the room temperature in the same manner as the dipping method (Fig. 2 (a)). The carrier tip was lifted up slightly from the drop of the electrolyte held by the Ni ring (Fig. 2 (b)). Then, about 5 μ L of toluene solu-

tion was added, which floated over the electrolyte (Fig. 2 (c)). In order to change the lifted up length (Fig. 3), a stage was used whose height can be adjusted by making 0.1 mm increments (SIGMAKOKI CO., LTD.). When the apex of the carrier tip was soaked in the toluene solution, the solution was pulled up by surface tension. Finally, the toluene solution was gradually evaporated, at which point the cone became narrow and broke off from constriction. The cone was defined as the shape of the toluene solution that linked the electrolyte to the apex of the carrier tip. In order to determine the optimal condition, both the concentration of the solution and the lifted up length were changed. The Ir complex utilized in this research has high probability to produce molecular ions, which reduces the number of ions detected per unit volume. Therefore, we defined the best condition in which the longest deposit length was obtained. First, the relationship between the concentration of the solution and the deposit length of the Ir complex on the apex of the tip was investigated. The concentrations of the toluene solutions used were 0.001 wt%, 0.01 wt% and 0.1 wt%. Additionally, the lifted up length (Fig. 2) from the electrolyte was also investigated by changing the length from 0.2 mm to 0.5 mm by making 0.1 mm increments using the manual stage; the relationship between the lifted up length and the deposit length was then determined.

III. RESULTS AND DISCUSSION

The radius of the curvature of the carrier tip prepared by electrolytic polishing is of several tens of nanometers. The carrier tip is likely to break even under a very weak impact; therefore, the carrier tip should be soaked in the solution in a direction perpendicular to the solution surface. However, this is difficult to perform consistently and requires some techniques. In contrast, the new method does not need such a procedure and even unskilled technicians can easily prepare the sample. Even if the carrier tip did not break, the Ir complex did not always adhere to the apex of the tip and mainly adhered to the side of the tip when using the previously reported method (Fig. 4 (a)). When applying the new method, the carrier tip seldom broke and the Ir complex often adhered to the apex of the carrier tip. The deposit was needle-shaped and a sufficient amount of the deposit was obtained for the analysis (Fig. 4 (b)). When the molecules mainly adhered to the side of the carrier tip, the amount of the deposit was not sufficient for the measurement. Therefore, optimum conditions need to be determined.

The deposit lengths on the carrier tip at each concentration are shown in Fig. 5. The results show that the deposit length was not necessarily proportional to the concentration of the solution, and a 0.01 wt% solution concentration produced the longest deposit length. When the result of the 0.1 wt% was compared with the result of a 0.001 wt%, the deposit length of the 0.1 wt% was longer than that of 0.001 wt% at the range from 0.3 mm to 0.5 mm. This result is simply derived from the amount of the Ir complex solvated in toluene. The result achieved by using the 0.01 wt% solution suggests that some parameters aside from the solution concentration affect the deposit length. Both the height of the constriction from the elec-

FIG. 2. Procedure of the new sample preparation; (a) Equipment for the new method (b) Lift up after electrolytic polishing (c) Deposition shaping of the guest molecules.

FIG. 3. The solution cone breaks off at the constriction.

FIG. 5. Relationship between the lifted up length and the deposit length, and relationship between the concentrations of the solutions and the deposit length.

FIG. 4. The shape of the tips after the dipping method and the new method (a) Dipping method: Ir complex mainly adhered to the side of the tip. (b) New method: Ir complex mainly adhered to the apex of the tip and sharp deposit was formed.

trolyte and the length that shrinks after separation at the site of constriction are thought to affect the deposit length. When the concentration of the solution is higher, the constriction is thought to break at a higher position than that achieved with lower concentrations. This is because the surface tension weakens and the amount of the solution above the constriction decreases as the concentration of the solution increases. After the separation at the site of constriction, the apex of the deposit shrinks as toluene evaporates (Fig. 6). The degree of the shrinking is thought to be larger with more dilute solutions. In the case of the 0.01 wt% solution, the effect of shrinking

FIG. 6. The shrinking of the deposit after the separation at the constriction.

was assumed to be lesser than the effect of changing the height of the constriction. Therefore, the result achieved by using the 0.01 wt% solution was longer than that of the 0.1 wt% solution.

The deposit length of the Ir complex tended to become shorter when the lifted up length became longer at the range from 0.3 to 0.5 mm. As the lifted up length became longer, the toluene solution on the carrier tip was thought to be weakly pulled down toward the electrolyte, thereby constricting the deposit. When the apex of the carrier tip was near the surface of the electrolyte, the apex was thinly

coated by the Ir complex at 0.2 mm. However, the apex of the carrier tip was considered to have been soaked in the toluene solution, causing the cone to become very small between the apex of the carrier tip and the electrolyte. Consequently, the deposit length is thought to become shorter.

In this research, the deposit length was controlled by changing two parameters: the lifted up length and the concentration of the solution used. When the concentration of the solution used was altered, the deposit lengths measured were not found to be proportional to the solution concentration value. The 0.01 wt% solution afforded the longest deposit length. In contrast, the deposit length was found to have a negative correlation with the lifted up length. The longest deposit length was obtained when the lifted up length was 0.3 mm.

IV. CONCLUSIONS

In this study, the shape of the apex of the carrier tip was not always sharp. However, the Ir complex mainly adhered to the apex of the tip and the carrier tip did not break. In order to control the shape of the deposit, the deposit length was optimized by changing both the lifted up length and the concentration of the solution used in the analysis. The deposit length was not necessarily in proportion to the concentration of the solution. When the lifted up length was increased from 0.3 to 0.5 mm, a negative correlation between the lifted up length and the deposit length was noted. These results indicate that the

shape of the tips coated by the Ir complex can be controlled to some extent by adjusting the lifted up length and by changing the concentration of the solution. In this study, a new sample preparation method was developed that showed that it is possible to analyze a sample without contamination by using a Ga ion beam, which can also induce a sharp shape. The amount of the sample required for this method is very small. It is also expected that this method will enable the analysis of small quantities of organic materials. In addition, this method suggests an easy sample preparation method for APT in comparison with the FIB processing method currently used. However, since this method uses the surface tension of the solution when constriction is formed, the type of material used will have an effect on surface tension. In order to apply this methodology for the analysis of other materials, the solubility of sample in solution and the affinity of the solution for carrier tips should be considered. The process of making carrier tips is the same as for conventional electrolytic polishing; moreover, the preparation of the materials for electrolytic polishing and the voltages are also known. This information is important for the application of our method to the analysis of other materials.

ACKNOWLEDGMENTS

In this study, Dr. B. Tomiyasu (The University of Tokyo) is gratefully acknowledged for many helpful discussions.

-
- [1] A. P. Kulkarni, C. J. Tonzola, A. Babel, and S. A. Jenekhe, *Chem. Mater.* **16**, 4556 (2004).
 - [2] J. Zaumseil and H. Sirringhaus, *Chem. Rev.* **107**, 1296 (2007).
 - [3] K. Takagi, S. Abe, T. Nagase, T. Kobayashi, and H. Naito, *J. Mater. Sci.: Mater. Electron.* **26**, 4463 (2015).
 - [4] K. D. M. Harris and J. M. Thomas, *J. Chem. Soc., Faraday Trans.* **86**, 2985 (1990).
 - [5] F. Panciera, K. Hoummada, M. Gregoire, M. Juhel, F. Lorut, N. Bicaïs, and D. Mangelinck, *Microel. Eng.* **107**, 167 (2013).
 - [6] H. Takamizawa, Y. Shimizu, K. Inoue, T. Toyama, F. Yano, A. Nishida, T. Mogami, N. Okada, M. Kato, H. Uchida, K. Kitamoto, T. Miyagi, J. Kato, and Y. Nagai, *Appl. Phys. Lett.* **100**, 253504 (2012).
 - [7] G. Binnig and C. F. Quate, *Phys. Rev. Lett.* **56**, 930 (1986).
 - [8] H. Hutter, C. Brunner, S. Nikolov, C. Mittermayer, and M. Grasserbauer, *J. Anal. Chem.* **355**, 585 (1996).
 - [9] J. S. Fletcher, N. P. Lockyer, S. Vaidyanathan, and J. C. Vickerman, *Anal. Chem.* **79**, 2199 (2007).
 - [10] O. Nishikawa, M. Taniguchi, and A. Ikai, *Appl. Surf. Sci.* **256**, 1210 (2009).
 - [11] K. Narayan, T. J. Prosa, J. Fu, T. F. Kelly, and S. Subramaniam, *J. Struct. Biol.* **178**, 98 (2012).
 - [12] L. M. Gordon and D. Joester, *Nature* **469**, 194 (2011).
 - [13] T. F. Kelly, O. Nishikawa, J. A. Panitz, and T. J. Prosa, *MRS Bull.* **34**, 744 (2009).
 - [14] B. Gault, F. Vurpillot, A. Bostel, A. Menand, and B. Deconihout, *Appl. Phys. Lett.* **86**, 094101 (2005).
 - [15] B. Deconihout, F. Vurpillot, B. Gault, G. D. Costa, M. Bouet, A. Bostel, D. Blavette, A. Hideur, G. Martel, and M. Brunel, *Surf. Interface Anal.* **39**, 278 (2007).
 - [16] G. L. Kellogg and T. T. Tsong, *J. Appl. Phys.* **51**, 1184 (1980).
 - [17] B. Gault, W. Yang, K. R. Ratinac, R. Zheng, F. Braet, and S. P. Ringer, *Langmuir*, **26**, 5291 (2010).
 - [18] Y. Zhang, and A. C. Hillier, *Anal. Chem.* **82**, 6139 (2010).
 - [19] M. K. Miller, K. F. Russell, K. Thompson, R. Alvis, and D. J. Larson, *Microsc. Microanal.* **13**, 428 (2007).
 - [20] M. K. Miller and K. F. Russell, *Ultramicroscopy* **107**, 761 (2007).
 - [21] K. Thompson, D. Lawrence, D. J. Larson, J. D. Olson, T. F. Kelly, and B. Gorman, *Ultramicroscopy* **107**, 131 (2007).