Three dimensional atom probe tomography of nanoscale thin films, interfaces and particles

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Three dimensional atom probe tomography of nanoscale thin films, interfaces and particles

by

Yi Zhang

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

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Iowa State University
Ames, Iowa
2009
Dedicated to my wife, my lovely daughter and our families
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ABSTRACT

This dissertation demonstrates our research effort dedicating to extend the application of 3DAPT technique to various new materials including nanoscale monolayers, thin films, interfaces and particles for the first time. Novel sample designs and preparation methods are developed in order to broaden the application of the technique into fundamentally new areas such as monolayers, organic/biomaterials, polymers and nanoparticles analysis. Samples including surface oxide layers, ionic monolayers, alkanethiol monolayers, electrodeposited polymers, nanoparticles and metal-metal interfaces were successfully analyzed for the first time. A new sample configuration is proposed as using electrodeposited polymers to encapsulate nanoscale analytes and to coat conventional atom probe tips. This design enables the technique to image varieties of new materials which can not be analyzed before. Using this approach gold nanoparticles about 1.4 ~ 2 nm were observed in the three dimensional reconstruction images. The results demonstrate the ability of modern APT technique in the new areas and inspire the future discoveries.
CHAPTER 1. INTRODUCTION

1.1 GENERAL INTRODUCTION

Atom probe tomography (APT) has been developed to characterize nanoscale features of materials. It is one of a few techniques with the single-atom sensitivity and high spatial resolution. APT utilizes field evaporation of surface atoms, along with reconstruction of the data collected from a time of flight (TOF) mass spectrometer and a position-sensitive detector, to reveal the spatial arrangement of atoms with a resolution of better than 0.3 nm in all three coordinate directions. Currently APT is the only experimental method that can provide both structural and compositional information for subsurface and buried features from a single experiment. It has been successfully applied in charactering microstructures of metals, metal alloys, ceramics and semiconductors. The studies have been focused mainly in determination of phase composition, solute segregation, precipitates and grain boundaries.

Although APT has achieved tremendous success in some areas, progress on thin films, coatings and organic/biological materials has been very limited. The difficulties lie in both sample preparation and data reconstruction. In sample preparation the target materials must be shaped into needlelike tips to facilitate surface evaporation under external voltages. The small end radius of the tips can greatly enhance the potential field strength near the surfaces up to the necessary 10−50 V/nm for field evaporation. In addition, the features of interest
must be precisely located near the tip apex region. Apex radiuses of typical atom probe tips used in our researches were less than 100 nm. Current sample preparation methods such as electropolishing, focused ion-beam (FIB) milling and mechanical cutting are not suitable for the analytes mentioned above. Electropolishing can typically only be applied to conductive materials such as metals and metal alloys. In FIB milling the sample needs to be exposed to gallium (Ga\(^{+}\)) ions\(^{11}\) which could alter the composition of subsurface regions and potentially damage the materials or coatings. The mechanical cutting method is hard to produce high quality tips at this scale. Therefore development of new sample preparation methods and sample designs especially for organic thin films and nanoparticles are of great importance to extend the analytical ability of atom probe microscopy\(^{6}\).

The difficulties in data reconstruction come from the irregular surface evaporation and more complex fragments that are produced. The position of individual atoms in the three dimensional images of the volumes of interest are reconstructed strictly according to the detection sequence of the corresponding ions. Ideally the surface atoms are peeled off layer by layer in evaporation so that the three dimensional data can be constructed from many of these two dimensional slices. Since the evaporation sequence of surface atoms depends on the potential field distribution which highly correlates to the geometric shape of the tip apex, tip quality heavily affects the date reconstruction. This is not severe in conventional metal, alloy and most of semiconductor analysis for subsurface and buried features in bulky materials since additional treatments can always be applied to remove surface irregulars. But
for analysis of monolayers, thin films/coatings and nanoparticles, new sample configurations and preparation methods must be developed creatively.

On the other hand, surface evaporation of nonmetallic materials is fundamentally different from the traditional systems. The ions evaporated from metallic materials are mainly charged single atoms\(^{10}\). But from poorly conductive materials such as semiconductors, organics, polymers and biomolecules, charged fragments containing multiple atoms are usually the main components in mass spectrums\(^9\). Interpreting the chemical compositions of fragments is more difficult than single atoms.

### 1.2 OBJECTIVE

The main goal of this work is to develop new sample configurations and preparation methods in order to advance the application of atom probe tomography into fundamentally new areas such as monolayers, organic/biomaterials, polymers and nanoparticles analysis. With recent innovations in instrumentation such as incorporation of fast electronics and laser pulsing system, analysis of new materials becomes possible by APT. However because of the lack of relevant developments in sample preparations, the application of the technique has been largely limited. For instance, the first attempt to analyze a biomaterial, unstained DNA has been made 30 years ago by Panitz with a field ion microscope\(^{12}\). But a single three dimensional image of any organic/biomaterials has not been achieved so far. The entire
history of organic/biological material atom probe analysis is composed of only a few of publications by several research groups\textsuperscript{12-18}.

The researches in the work will be focusing on the following aspects: to modify and improve the conventional sample preparation method; to construct variety of monolayers on the metal surfaces as model systems for APT analysis; to prepare thin films and coatings from variety of polymers on the metal tip surfaces to achieve three dimensional analysis of the organic materials for the first time; to propose a novel sample design for nanoparticles analysis which can drastically extend the ability of the techniques to variety of new nanoscale analytes; to investigate the surface reaction mechanism from the interfacial analysis with atom probe microscopy. The results will demonstrate the ability of modern APT technique in the new areas and inspire the future discoveries.

1.3 THESIS ORGANIZATION

Background and example analysis with atom probe tomography will be illustrated in Chapter 2. Then variety of monolayers will be analyzed with APT in Chapter 3. In Chapter 4 several polymers will be investigated with APT. The polymers will be delivered onto the surfaces of metals tips by different means. The data qualities of atom probe tomography from the resulting films will be evaluated. In Chapter 5 a novel sample design for nanoparticle analysis will be developed. The polymer encapsulated nanoparticles will be prepared for analysis. In Chapter 6, interfacial analysis of copper coated aluminum tips will be performed.
The spatial and compositional information within the interfaces will be used to determine the mechanism of the deposition reactions.

**1.4 REFERENCES**


CHAPTER 2. INTRODUCTION TO ATOM PROBE TOMOGRAPHY

2.1 History

The development of the atom probe tomography has a long history since the discovery of electron emission from a solid by quantum tunneling. Many improvements have been made to the design of atom probe microscopes since then. Modern APT incorporates variety of new technologies such as high speed digital timing systems, position-sensitive single atom detectors and fast laser pulsing systems. A list of milestones in the development of the technique is illustrated in the table beneath.

Table 2.1. Development history of the atom probe technique.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Year</th>
<th>Inventors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field emission microscope</td>
<td>1936</td>
<td>Müller¹</td>
</tr>
<tr>
<td>Field ion microscope</td>
<td>1955</td>
<td>Müller²,³</td>
</tr>
<tr>
<td>Atom probe field ion microscope</td>
<td>1967~1968</td>
<td>Müller and Panitz⁴,⁵</td>
</tr>
<tr>
<td>Pulsed-laser atom probe</td>
<td>1970s-present</td>
<td>Tsong et al.⁶-¹²</td>
</tr>
<tr>
<td>Three dimensional atom probe</td>
<td>1980s</td>
<td>Miller et al.¹³-¹⁶</td>
</tr>
<tr>
<td>Local electrode atom probe</td>
<td>1994-present</td>
<td>Nishikawa¹⁶,¹⁷, Kelly et al.¹⁸</td>
</tr>
</tbody>
</table>

The direct ancestors of three-dimensional atom probe tomography (3DAPT) are the field emission microscope (FEM) and field ion microscope (FIM). E. W. Mueller invented the first FEM in 1936 at Technical University of Berlin, Germany. Under negative potential, electrons were emitted along the direction normal to the surface of a sharp metal needle by
quantum mechanical tunneling and projected onto a phosphor screen, forming an image of the surface atom arrangement. It achieved a spatial resolution of 2 nm and the magnification of the order of 10^4. This was the first surface analytical technique enabling people to examine the various properties of the solid surfaces such as surface diffusion and migration.

The first image of individual atoms by any technique was achieved from a FIM invented by Bahadur and Müller at Pennsylvania State University on October 1955. A sharp tungsten needle was placed in front of a phosphor screen in vacuum and cooled to cryogenic temperatures. The polarity of the specimen was changed from negative to positive potential while introducing an image gas into the vacuum. When approaching the surface atoms of the tip, the gas atoms were field ionized by quantum mechanical tunneling of the outmost electron in the gas to the metal tip under high potential field. This continuously tunneling process from individual atom sites formed stable emitting sources. The gas ions eventually hit the detector and were neutralized at ground potential. The detected imaging gas ions revealed a projection image of the arrangement of the surface atoms.

In FEM or FIM, surface atoms of the specimen generally do not leave the surface, despite they may move along the surface because of surface diffusion. In 1956 the important discovery of field evaporation discovered by Müller made it possible to develop atom probe microscope. Field evaporation refers to the phenomena that surface atoms can sublime from the material under high field strength. With careful control on field strength, surface atoms can be precisely removed in a one by one fashion. In 1967 and 1968, in order to identify the
ions imaged in the FIM, Müller and Panitz developed the first atom probe microscope. It was a combination of a field ion microscope and a mass spectrometer. The ions being field evaporated in the FIM were detected by the mass spectrometer to identify their compositions.

In most of atom probe analysis voltage pulses have been used to field evaporate atoms from samples. However this also limits the applications of the technique to metals since the sample materials must have electrical conductivity greater than $10^2$ S/cm to deliver the pulse to the sample apex effectively\textsuperscript{21}. In 1970s some researches have started to seek alternative approaches for surface ionization by using laser pulses. Despite the advantages of pulsed laser evaporation, the technique has not been developed until recently because of the difficulties of aligning the laser beam and lack of understanding in the background mechanism. Thus most of the early applications have been focused on photo-dissociation of adsorbed molecules on the tip surfaces. Since 2002 with the increasing demands on semiconducting and insulating material analysis, and advances in modern laser technology, fast laser pulsing systems have been incorporated into the atom probe technique. The first commercial pulsed-laser atom probe was developed in 2006 by Imago Scientific instruments and Cameca SA. This improvement enables the technique for more potential application such as organic and biomaterial analysis.

In the 1980s a series of atom probe microscopes with three-dimensional imaging ability were developed. The ions are evaporated either by voltage pulse or by laser pulses one at a time and their x-y positions are recorded by a two-dimensional position-sensitive
detector. With the right geometrical shape of the sample, the surface atoms are peeled off layer by layer. The sequence of the ion hits are used to determine their positions in a given layer and also the positions of different layers. With the aid of computer the three-dimensional image can be constructed from all of the two-dimensional slices. Therefore the new technique is generally called atom probe tomography (APT). This evolution makes the technique an unparallel approach for analyzing important bulk properties such as grain boundaries, interfaces and phase segregation. The APT can achieve \(< 0.3 \) nm resolutions in all the three directions\(^1\).

The most recent modification to the atom probe technique is the incorporation of the local electrode. This design can significantly reduce the imposed voltage because of shorter distance between the tip and electrode and enhancement of the potential field. The original idea was proposed by Nishikawa and Kimoto in 1994\(^2\). Kelly et al. recognized the local effects of the counter electrode with the samples and developed a local electrode atom probe (LEAP). In this configuration the cooled needle-shaped sample is mounted on a micropositioning stage and pointed towards a funnel-shaped local electrode. The apex of the sample is aligned to the aperture in the local electrode. Since the sample is brought much closer to the aperture, the field of view is also largely extended.
2.2 Principle and Instrumentation

From the development history of the atom probe microscope one can see that the technique is a combination of some other techniques including FIM, mass spectrometer, position-sensitive single atom detector, fast laser and voltage pulsing systems, high speed electronics, reconstruction and analysis software packages. It’s expected that more advanced techniques will be introduced in the future development. For end users, some basic knowledge about background principles and instrumentation is needed before proper analysis being carried out.

In principle, the atom probe microscope is a combination of a field ion microscope and a mass spectrometer. The key components along the detection route of a single ion include a local counter electrode (LE), a microchannel plate (MCP) amplifier and a position-sensitive detector, as shown in Fig. 2.1. The surface atoms of the sample are evaporated by superimposed voltage or laser pulsing. After leaving the surface they pass the aperture in the local electrode and enter the field free region where their times of flights are recorded by the mass spectrometer. Then the individual ion hits the microchannel plate (MCP) and the signal is magnified strong enough to be detected by the multi-anode position-sensitive detector. The X-Y positions of ions and their hitting sequence are recorded along with their chemical identities determined by the mass spectrometer. With the spatial and compositional information the evaporated volume can be reconstructed.
Figure 2.1. Schematic diagram of a local-electrode atom probe (LEAP) microscope. The surface atoms of the sample are evaporated by superimposed voltage or laser pulsing. After leaving the surface they pass the aperture in the local electrode and enter the field free region where their times of flights are recorded by the mass spectrometer. Then the individual ion hits the microchannel plate (MCP) and the signal is magnified strong enough to be detected by the multi-anode position-sensitive detector. The X-Y positions of ions and their hitting sequence are recorded along with their chemical identities determined by the mass spectrometer. With the spatial and compositional information the evaporated volume can be reconstructed.

*MCP: Microchannel Plate*
Surface atom evaporation is carried out by two methods: voltage induced field evaporation and laser induced evaporation. The former method requires the tested material to be electrical conductive in order to provide sufficient potential strength to the surface for evaporation. The latter method undergoes a different mechanism which can be used to evaporate insulating materials.

Field evaporation is the phenomenon that under an external field the ionic state of an atom becomes more stable than its neutral state at a specific distance from the surface. The process is illustrated in Figure 2.2. The atomic curve shows the potential energy distribution without external potential field. After the external potential being introduced, the potential energy distribution shifts to the ionic curve. From a specific distance away the surface the ionic curve has lower potential energy than the atomic curve where the ionization occurs. In the atom probe microscope after the surface atom being ionized into Mn+ ion it will be evaporated from the positively charged surface.

Figure 2.2. Potential energy diagram illustrating the mechanism of field evaporation. The X coordinate refers to the distance from the surface.
Laser induced evaporation has a different mechanism from field evaporation although the details are still under debate. One explanation is that the electronic excitation or thermal heating by the laser energy facilitates surface atoms to be ionized and overcome the ionization energy barrier. Another explanation is that the field evaporation is induced by the electrical field component of the laser beam. Both theories have experimental support from specific materials, but the thermal heating seems predominant in most situations. Laser induced field evaporation has some advantages over voltage pulsing. It reduces the stress produced by the high voltage applied therefore lowers the possibility of specimen fracture. For some materials having low electrical conductivities, total external voltage needs to be very large to obtain sufficient field strength without the aid of laser. For some insulating materials, voltage induced field evaporation becomes impossible, which limits the application of 3DAP on some important materials such as semiconductors, ceramics, polymers and biological systems. However voltage induced evaporation is much easier to carry out for metallic materials by avoiding complicated alignment and focus steps.

The time of flight mass spectrometer is used to determine the chemical identity of the ions according to their mass to charge ratios. The mass is proportional to the square of the time of flight passing the field free zone, as demonstrated in equation (2-1):

$$\frac{m}{n} = 1.9297 \times 10^{-4} \left( \alpha V_{DC} + \beta V_{pulse} \right) \frac{(t - \tau)^2}{\delta^2}$$ (2-1)
\( t \) is the TOF in nanoseconds. \( \tau \) is the correction term that takes into account the delay of the signal transmission in cables and electronics. \( \delta \) is the estimate of the flight distance in millimeters. \( \alpha \) and \( \beta \) are the corrections for \( V_{dc} \) and \( V_{pulse} \) respectively.

In the modern atom probe microscope, the surface atoms are precisely controlled to evaporate one at a time. The surface of the sample is peeled off layer by layer. After a single ion passing the mass spectrometer and hitting the microchannel plate (MCP), millions of secondary electrons are generated from the walls of the channels and hit the position-sensitive detector. The corresponding X-Y position is recorded for the incident ion along with its chemical identity. The series of ions are detected and recorded in each pulse and a sequence of hitting history is obtained. The sequence composed of millions of hitting records is used to reconstruct the three dimensional image. The X-Y positions in the record are used to identify the original locations of the atoms in the layer. The types of atoms are coded according to their chemical identities. The sequence of hitting atoms is used to locate the atoms in the same layer and to identify the order of layers as well. Thousands of two dimensional slices are then used to construct the three dimensional image.

2.3 Current Applications and Limitations

The atom probe microscopy has been successfully applied in charactering microstructures of metals\(^{25,26} \), metal alloys\(^{27-44} \), ceramics\(^{45-51} \), superconductors\(^{52} \) and semiconductors\(^{53-59} \) since its invention over 30 years ago. The analyses have been mainly
focused on determination of phase composition, solute segregation, precipitates and grain boundaries in the subsurface or buried volumes.

Since the first working atom probe microscope with incorporated laser pulsing system was developed only until 2002, the early applications before this have been highly concentrated in the area of metallic systems. With the development of three-dimensional imaging ability, the atom probe microscope becomes an unparallel tool to reveal the nanoscale spatial and compositional information of the materials. Variety of important metal alloys has been investigated by the APT to provide direct observations and evidences to help explain their macroscopic behaviors. Here some important examples are worth while to be mentioned. For example, the pressure vessels used in nuclear reactors have been investigated by the technique to explain the material embrittlement. The performance deterioration was thought because of the interaction of solutes with the vacancies and other products created by the incident neutrons. The 3D imaging from APT analysis on the alloys has helped to discover that the material failures were contributed by ultrafine copper-enriched precipitates, phosphorus clusters, segregation to dislocations and grain boundaries. Lots of studies have shown that APT is a powerful tool to investigate bulk properties of materials which can not be easily achieved by any other techniques. A 3D image of a piece of heat-resistant ferritic steel was reconstructed by a researcher from Imago Scientific Instruments and illustrated in Figure 2.3. The coherent (Ni,Fe) AI precipitates (noted in the upper image as $\alpha_1$, $\alpha_2$ and secondary $\alpha_1$) in a ferritic matrix are used to achieve good high temperature mechanical
properties. Detailed features on the nanoscale are clearly observable in the reconstruction image, which is not a trivial task in any other techniques.

Figure 2.3. Three dimensional image of a piece of heat-resistant ferritic steel obtained from atom probe analysis. The coherent (Ni,Fe) Al precipitates (noted in the upper image as $\alpha_1$, $\alpha_2$ and secondary $\alpha_1$) in a ferritic matrix are used to achieve good high temperature mechanical properties. The elements including Al, Cr, Fe and Ni are coded by different colors. The corresponding atomic concentration distributions of all elements are readily calculated in the lower graph. Data courtesy of C. Stallybrass, G. Sauthoff, A. Schneider, Y. Degas (Max Planck Institute Düsseldorf) and D. J. Larson (Imago).

The introduction of modern fast laser pulse system in 2002 drastically extends the ability of the atom probe technique and leads the potential applications to a variety of whole new areas including semiconductors, oxides, organic materials and biological systems.
Emerging demands in revealing the microstructures and trace element distributions in these materials have been limited by lack of proper tool with sub-nanoscale resolution and three-dimensional imaging ability. Only a few years after the development of the new generation atom probe microscope promising progresses have been made in analysis of semiconducting materials. A study on the silicon defects induced nonuniform distribution of low concentration dopant atoms with APT provides the quantitative evidences to answer the critical question for developing nanoscale semiconductor field-effect devices\textsuperscript{62}. The controlled placement of trace amount of dopant atoms in Si is a fundamental process in semiconductor device fabrication. But in the process defects in Si crystal lattices are also developed which will disturb the implantation of the dopants. Direct observations and quantitative analysis of the phenomenon has not been achieved before. With the help of laser-assisted atom probe tomography, three-dimensional mapping of individual dopant and other impurity atoms within Si was obtained (Figure 2.4). Fig. 2.4a is the TEM image showing the As-rich defect region and the end-of-range damage layer. The 3D image from atom probe tomography (Fig. 2.4b) shows a spheroid-shaped dopant (As)-rich defect region enclosed in the purple isoconcentration surfaces. The results provide detailed 3D view of the actual placements of the dopant atoms in the semiconductive materials.
Figure 2.4. TEM and Three dimensional atom probe imaging of the dopant (As)-enriched regions in the Si. TEM (a) shows the As-rich defect regions and the end-of-range damage layer. The 3D image from atom probe tomography (b) shows spheroid-shaped dopant(As)-rich defect region enclosed in the purple isoconcentration surfaces. Oxygen atom isoconcentration surfaces are colored in blue. The mass spectrum from the analysis is provided in (c).

Despite the achievements in metallic and semiconductive material analysis, very limited progress has been made on organic and biological materials in the past 30 years. In 1975 2D field ion microscopy (FIM) images of freeze-dried tRNA dimers were reported with a resolution of 1~2 nm. In the 1980s, some biological materials including ferritin and
unstained DNA\textsuperscript{65} were imaged by the FIM. In the 1990s, a few researches on carbon films\textsuperscript{66,67}, graphite fibers\textsuperscript{68}, polypyrrole\textsuperscript{69} and pyrthalocyanine\textsuperscript{70} were reported analyzed by FIM. These are basically all the history of organic and biomaterials analysis with field ion microscopy. After the development of atom probe microscopes, no report has been published as to our best knowledge.

As mentioned in the previous chapter, the difficulties in extending the ability of the techniques lie in both sample preparation and data reconstruction. Conventionally the target materials must be shaped into the needlelike tips for analysis to facilitate surface evaporation under external voltages which is unfeasible under some circumstances. For instance, lots of organic or biomaterials have very low mechanical strength and poor electrical conductivities, which make some traditional sample preparation methods such as mechanical polishing and electropolishing unusable. These materials are also highly sensitive to radical treatments such as focused ion beam milling. On the other hand, the features of interest must be precisely located near the tip apex region. Apex radiuses of typical atom probe tips are less than 100 nm. Since direct sample preparation from these materials is difficult, they must be delivered to the small analyzable regions. Therefore development of new sample preparation methods and sample designs especially for organic thin films and nanoparticles which are simple enough to transfer the analytes from variety of mediums into analyzable regions are of great importance to extend the analytical ability of atom probe microscopy\textsuperscript{71}. 
The difficulties in data reconstruction come from the irregular surface evaporation and more complex fragments that are produced. The position of individual atoms in the three dimensional images of the volumes of interest are reconstructed strictly according to the detection sequence of the corresponding ions. Ideally the surface atoms are peeled off layer by layer in evaporation so that the three dimensional data can be constructed from many of these two dimensional slices. Since the evaporation sequence of surface atoms depends on the potential field distribution which highly correlates to the geometric shape of the tip apex, tip quality heavily affects the date reconstruction. This is not severe in conventional metal, alloy and most of semiconductor analysis for subsurface and buried features in bulky materials since additional treatments can always be applied to remove surface irregulars. But for analysis of monolayers, thin films/coatings and nanoparticles new sample configurations and preparation methods must be developed creatively.

On the other hand, surface evaporation of nonmetallic materials is fundamentally different from the traditional systems. The ions evaporated from metallic materials are mainly charged single atoms\(^2\). But from poorly conductive materials such as semiconductors, organics, polymers and biomolecules, charged fragments containing multiple atoms are usually the main components in mass spectrums\(^3\). Interpreting the chemical compositions of fragments is more difficult than single atoms.
2.4 Development of Electropolisher

In most of our researches, conventional needle-like tips will be used as substrates to form complex configurations such as thin films and coatings. Organic materials and nanoparticles are also delivered onto the metal tip apex by variety of methods. Developing a simple method for metal tip preparation is the first step. Electropolishing is a suitable approach for routine sample preparation from variety of metal wires and sheets. Required instrumentation is usually much simpler than other methods such as focused ion beam milling. The quality of the sample made from electropolishing is suitable for most applications.

A homemade electropolisher was developed as illustrated in Fig 2.5. Specimens were prepared by electropolishing of metal wires. Typically a piece of 0.2 mm diameter metal wire was cut into 10 mm long and clamped at one end in a copper tube. A platinum ring electrode was mounted on the vertical arm of motorized stage and served as the counter electrode in a two-electrode electrochemical cell. The metal wire was aligned into the ring perpendicularly. The polishing fluid used here consisted of 25% (v%) perchloric acid and (70%) glacial acetic acid. A reservoir containing the fluid was placed right under the loop for refreshing the liquid retained in the loop by periodically dipping the loop into the fluid. The fluid in the loop formed a thin layer as the electrolytic cell so the metal wires could be immersed in the liquid film. The movement of the ring electrode was controlled by Labview program. The DC voltage exerted on the metal wire was carefully adjusted according to the type of material to
Figure 2.5. Schematic diagram of the homemade electropolisher. (A) Before start of electropolishing, the ring electrode is dipped into fresh-made polishing fluid. A film of the liquid is formed in the ring as electrolyte cell. The liquid is also periodically refreshed after several cycles of polishing. (B) During electropolishing, materials are removed from a wire in the polishing fluid under the applied voltage $V_{DC}$. The ring electrode removes reciprocally to help remove dissolved materials near the wire surface. A neck region is formed gradually. (C) When the neck becomes thin enough, the wire is broken by gravity. Therefore two needlelike tips are obtained.
obtain proper etching speed and suppress bubble generation. During electropolishing, the ring electrode was moved up and down in a small range to help remove the material. After several cycles of polishing, the ring was dipped into the reservoir to refresh the fluid. During the etching process, material of the wire was dissolved gradually to form a neck region in the wire. This region became thinner and eventually was fractured by its own weight. Then DC voltage was turned off immediately. Two sharp tips were obtained: the upper one stayed on the stage while the lower one dropped in the reservoir.

With this electropolisher we have successfully made over 800 tips with smooth surfaces and tip radius < 100 nm from several metals including aluminum, stainless steel, gold and. The etching conditions are listed in Table 2.2.

<table>
<thead>
<tr>
<th>Tip material</th>
<th>Etching Voltage (VDC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>11.5~12.5</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>5.5~7</td>
</tr>
<tr>
<td>Gold</td>
<td>5~8</td>
</tr>
<tr>
<td>Palladium</td>
<td>4~5</td>
</tr>
</tbody>
</table>

Table 2.2. Etching conditions for different materials by homemade electro-polishing workstation.

To check quality of tips, they were first inspected under an optical microscope. The optical images of several different tip materials are given in Fig. 2.6. The resulting tips have straight and sharp end with smooth outer surfaces, which ensures appropriate evaporation sequences and good image reconstructions. The well defined shape of the tip also serves as a good substrate for consequent deposition or coating layers. The electropolisher can be used to
prepare tips from much wider collections of materials by using proper fluid recipes and carefully adjusting the etching voltages.

Figure 2.6. Optical images of fresh made specimens by aluminum (a, b), stainless steel (c, d) and palladium (e, f). The magnification is $20 \times$ in (a, c, e), and $50 \times$ in (b, d, f).
Surface conditions in the tip apex can be checked by the field ion microscope and atom probe microscope. Some images are given in Fig. 2.7. In the FIM image of aluminum (Fig. 2.7a), an fcc single crystal surface was presented with several sets of concentric rings. They formed a 3-fold symmetry pattern. Those rings correspond to the edges of crystal planes where the image gas was preferentially ionized. A (111) plane located off the center surrounded by rings of (200), (020) and (220) planes. The similar structure was found in a cumulative hit record from the atom probe microscope (Fig. 2.7b). The FIM image of stainless steel tip (Fig. 2.7d) did not show lattice planes as in the aluminum tip, indicating the amorphous structure of its surface. The atom probe image (Fig. 2.7e) did not show obvious crystal structure either. The FIM of palladium tip (Fig. 2.7g) revealed ring-like feature indicating its fcc single crystal surface. They also formed a 3-fold symmetry pattern as in aluminum. A (111) plane located in the center of the image, surrounded by (200), (020), (002), (220), (202) and (022) planes. At the same time, some random distributed bright dots presented in the graph, which may be metal oxides or adsorbates such as H₂O and CO. In its atom probe image (Fig. 2.7h), the first several hundred hits in the detector screen showed the exact ring structure in the center with same size as in (Fig. 2.7g). But other rings in the FIM image were invisible here since only several hundred of hits were collected.

The corresponding mass spectrums (Fig. 2.7c, f and i) from surface evaporations in atom probe analysis (Fig. 2.7b, e and h) are also given respectively. For the pure materials such as Al ((Fig. 2.7b and c) and Pd (Fig. 2.7h and i), only characteristic peaks of the metals
Figure 2.7. Images of specimens made from aluminum (a, b, c), stainless steel (d, e, f) and palladium (g, h, i). The images were obtained by FIM (a, d, g) and atom probe microscope (b, e, h). The mass spectrum from the three atom probe runs were shown in (c, f, i). He was used as image gas in FIM imaging. The temperature of specimen was maintained at 30 K during field ion imaging. The $V_{DC}$ was adjusted to achieve clear images. In LEAP imaging the temperature of specimen was kept at 50 K. Laser pulse with 0.1 nJ pulsing energy was applied on the specimen to excite surface atom evaporation. The cumulative hit records were used here as the images. Blue dots represented detected hitting events.
appear in the mass spectrums. In Fig. 2.7c, single peak found at 27 (u/e) is composed of the hits of $^{27}\text{Al}^+$ ions. In Fig. 2.7i, six isotones of palladium with atomic weight 102, 104, 105, 106, 108 and 110 (g/mole) appear as a group of peaks within 102 ~ 110 (u/e). These peaks correspond to the single charged Pd$^+$ ions. Another set of peaks found in 51 ~ 55 (u/e) are the double charged Pd$^{2+}$ ions. In Fig. 2.7f, Stainless steel shows variety of peaks in a broader range indicating its multiple components. Fe$^{2+}$, Ni$^+$, Ni$^{2+}$, CrP$^+$, Mn$^+$ and Co$^+$ are found in the mass spectrum. The mass spectrums are collected simultaneously with ion position detection. Unlike in normal mass spectrometry, each ion in the peaks has positional information which will be used in three dimensional image reconstructions.

The operating voltages in FIM and LEAP imaging are given in Table 2.3.

Table 2.3. The experimental conditions in field ion imaging and LEAP imaging from the three materials. The laser pulse energy used in the tests was all set to 0.5 nJ for the three materials.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Applied Voltage (V)</th>
<th>Specimen Temperature (K)</th>
<th>Applied Voltage (V)</th>
<th>Specimen Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>5239</td>
<td>32.4</td>
<td>3256</td>
<td>54.3</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>8530</td>
<td>32.3</td>
<td>7134</td>
<td>50.9</td>
</tr>
<tr>
<td>Palladium</td>
<td>2713</td>
<td>32.3</td>
<td>3255</td>
<td>53.3</td>
</tr>
</tbody>
</table>

FIM imaging and atom probe imaging were carried out on the same tip made from each material. Laser assisted evaporation was used in all the atom probe tests. The laser pulse energy used in the tests was all set to 0.5 nJ for the three materials. From the applied voltages
and operating temperatures we can see that atom probe imaging were generally run under more modest conditions with lower external voltages and higher cryo temperatures. Lower testing voltage reduces the potential induced tip fractures. Higher temperature also reduces the possibility of sample fractures. The advantages of LEAP microscope come from the incorporation of the local electrode and application of the laser pulses. Local electrode significantly shortens the distance between the tip and the counter electrode therefore drastically enhances the potential field strength under similar external voltages. Fast laser pulses provide additional thermal energy for surface evaporation so reduce the required field strength.

2.5 An Example of 3D Image Reconstruction

In this section a full atom probe analysis on a conventional metal tip (made of Pd) will be demonstrated. Firstly an optical image in Fig. 2.8 shows the palladium tip made from the homemade electropolisher, having a straight and sharp end and smooth outer surface. The tip can be readily examined by the atom probe microscope.
Figure 2.8. Optical images of a fresh palladium tip prepared by electrochemical polishing. The big image was taken under 20X magnification, while the insert under 50X. The Pd tip was etched from a piece of Pd wire (0.2 mm diameter) in the homemade electropolisher. The etching fluid was prepared by mixing 3 parts of glacial acetic acid with 1 part perchloric acid. Potential difference for polishing was 5 V.

Voltage and mass history recorded from a test with laser pulse are given in Fig. 2.9. Voltage in voltage history (Fig. 2.9a) was increasing corresponding to the tip radius increment as the topmost materials being removed and the surface moving down. At the same time, the chemical identities of ions were resolved by the time of flight mass spectrometer and recorded in the mass history (Fig. 2.9b). In the mass history, the detected ions are recorded along the surface evaporation. The ions appearing in earlier part are from the region more close to the initial tip surface. Light and complex ions are found in this region including HO+, H2O+, H3O+ and Pd(H2O)+, indicating water residuals are left on the tip surface after rinsing. With the evaporation proceeding, the amount of these ions decreases. But since the residuals are also adsorbed on the side surface of the tip, these ions still appear in the later part of evaporation.
Figure 2.9. Voltage (a) and mass spectrum (b) history recorded from an atom probe analysis on a fresh made Pd tip. Voltage was increasing trend because of growth of the radius of evaporation frontier.

After sufficient amount of ions was collected the field evaporated was terminated.

The accumulative mass spectrum (Fig. 2.10) was obtained. Location of the peaks in the mass spectrum was used to identify presence of the metal ions. Relative sizes of their peaks were expected to be proportional to their natural abundance. Two groups of peaks were found in the mass spectrum. Pd has six isotopes at atomic mass of 102, 104, 105, 106, 108 and 110,
which are corresponding to the group of six peaks for Pd$^+$ ions in the same positions. Peaks appeared at mass to charge ratios of 51, 52, 52.5, 53, 54 and 55 verify presence of Pd$^{2+}$ ions. The nature abundance ratios of the isotopes are 1.02%, 11.14%, 22.33%, 27.33%, 26.46% and 11.72. The detected abundance ratios for the isotones were 1.03%, 11.05%, 22.28%, 27.36%, 26.46% and 11.82%, all within 0.9% deviation showing high detection ability of the technique.

After the chemical identities of individual ions were determined, computer software was used to reconstruct the 3D image of analyzed volume. Briefly while the surface of the Pd
tip was peeled off atom by atom along the evaporation going on, the X-Y position of individual was recorded along with its mass to charge ratio. The series of ions were detected and recorded in each pulse and a sequence of hitting history was obtained. The sequence composed of millions of hitting records was used to reconstruct the three dimensional image of the evaporated volume. The X-Y positions in the record were used to identify the original locations of the atoms in a layer. The sequence of hitting atoms was used to locate the atoms in the same layer and to identify the order of layers as well. The types of atoms were determined as mentioned in previous paragraph and coded according to their chemical identities. Thousands of two dimensional slices were then used to construct the three dimensional image (Fig. 2.13c).

Detailed reconstruction process is illustrated in Figure 2.11 and Figure 2.12. The whole process can be divided into two steps: data conversion, and image reconstruction. In data conversion, several corrections are applied on the raw experimental data, including voltage and flight path corrections for converting raw time-of-flight $\text{TOF}_{\text{RAW}}$ to corrected $\text{TOF}$, geometric conversion for determining ion original positions $(X, Y, Z)$ from detector positions $(X_D, Y_D)$ and evaporation sequence. In image reconstruction, the corrected data is used to reconstruct the three dimensional image of analyzed volume as described in previous paragraph from original positions and chemical identities of ions.
Figure 2.11. Flow chart of experimental data reconstruction. Raw data contain all the hits for surface evaporation. Each hit record includes its sequence number, sample voltage, raw time of flight ($\text{TOF}_{\text{RAW}}$) and detector position ($X_D$, $Y_D$). $\text{TOF}_{\text{RAW}}$ is converted to corrected TOF by applying voltage and flight path corrections iteratively. Corrected TOFs are converted to mass-to-charge ratios. Atoms’ original positions are calculated in geometric reconstruction and illustrated in details in Figure 2.12.
Voltage and flight path corrections on TOF\textsubscript{RAW} are explained in Fig. 2.11. TOF value of each hit is used to determine the mass-to-charge ratio (m/n) which will be used to identify the chemical composition of the detected ion. Because the ions from different depth in the sample are evaporated under changing voltage V\textsubscript{DC}, voltage correction is necessary to remove the TOF dependence on the voltage. A semi-empirical relationship is normally used:

\[ t = \frac{a_o}{\sqrt{a_1 + V_{DC} + a_2 V_{DC}^2}} \]  \hspace{1cm} (2-2)

where t is the time of flight, a\textsubscript{0}\textasciitilde a\textsubscript{2} are empirical parameters, V\textsubscript{DC} is the voltage. The spectrum of TOF\textsubscript{RAW} and corrected TOF spectrum can be found in Fig. 2.11 as well. At the same time, flight path correction is also applied on the spectrum of TOF\textsubscript{RAW}. It eliminate TOF variations for a given m/n value and voltage configuration, arising from differences in path-length trajectories. This correction is determined by computing the average flight time for a given m/n value as a function of the ion impact position (X\textsubscript{D}, Y\textsubscript{D}) on the detector and fitting this average to an empirical function f(X\textsubscript{D}, Y\textsubscript{D}). In practice, the two corrections are performed iteratively until the variation is acceptable. After the voltage and flight path correction, the mass-to-charge ratio m/n can be determined for the corrected TOF with the relationship (2-3):

\[ m/ n = 2eVt^2 / L^2 \]  \hspace{1cm} (2-3)

The relationship between TOF (t) and m/n can be found in Fig. 2.11. m/n is consecutively used to identify the type of ions. L is the flight length.
The original positions \((X, Y, Z)\) of the detected ions before being evaporated is determined through the geometric reconstruction as illustrated in Figure 2.12. \((X, Y, Z)_s\) is determined from detector position \((X_D, Y_D)_s\), the sequence number and some other factors. The sample radius can be estimated from \(V_{DC}\) by equation (2-4):

\[
r = \frac{V_{DC}}{k \cdot F_e}
\]

where \(r\) is the tip radius, \(k\) is a geometric factor and \(F_e\) is evaporation potential. For the conical tip, \(k\) was set to equal 3.5.

Figure 2.12. Schematic chart of geometric reconstruction of analyzed volume. The original position of each detected ion is determined by its detector position \((X_D, Y_D)\), its sequence number and some other factors. With these spatial information, the three dimensional image of the analyzed volume can be reconstructed.

The magnification is determined by:

\[
M = \frac{S}{s_0} = \frac{(L + \xi R)}{\xi R} \approx \frac{L}{\xi R}
\]

(2-5)
where $M$ is the magnification, $S$ is the spacing on detector, $s_o$ is the spacing in the sample, $L$ is the flight length, $\xi R$ is the reconstruction center. The magnification of APT is about $10^6$ for mm/nm.

The original $X$, $Y$ coordinates in sample are determined from the detector position $(X_D, Y_D)$ and the magnification as in (2-6):

$$X = \frac{X_D}{M} \quad \text{and} \quad Y = \frac{Y_D}{M} \quad \text{(2-6)}$$

The $Z$ coordinate, the depth direction, is calculated from evaporation sequence and volume increment as in (2-7).

$$Z = Z_0 + \delta Z = Z_{\text{initial}} + \frac{\text{atom volume}}{(\text{detector efficiency}) \times (\text{surface area})} \quad \text{(2-7)}$$

A more careful dimensional calibration is usually necessary after the first 3D image is obtained. For metal crystals it’s convenient to use the lattice spacing parameters from variety of sources as the factor for dimensional calibration. Since the palladium tip was made from crystallized metal wire, lattice planes were expected from the 3D image. The TEM image in Fig. 2.13a&b shows that lattice spacing is 0.225 nm. Based on the direction of (111) plane in FIM image of Pd tip (Fig. 2.7e), we found that it was perpendicular to the tip axle or evaporation direction. So the spacing from TEM was thought to be between (111) planes.

A theoretic value of lattice spacing can be calculated as well. Since the diameter of a Pd atom is reported as 0.389 nm$^{72}$. The lattice spacing along the axial direction of the Pd tip
Figure 2.13. Nanoscale images of two bare palladium tips from TEM (a, b) and data reconstruction of 3D atom probe microscopy (c, d). For TEM imaging, the Pd tip was intentionally blunted for better resolving crystal lattice layers (A). From the image of higher magnification the lattice spacing are visible to be about 0.2 nm (b). Three dimensional reconstructed image of a sharp Pd tips is presented in (c). The insert in the
zoomed in image (d) showed that the lattice spacing were about 0.2~0.3 nm, agreed with that from TEM images.

is the distance between two adjacent (111) planes. The spacing can be calculated by the following equation (2-8):

\[ d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{0.389 \text{ nm}}{\sqrt{1^2 + 1^2 + 1^2}} = 0.225 \text{ nm} \]  \hspace{1cm} (2-8)

The lattice spacing of 0.225 nm was used for calibration. A trial and error procedure was applied in dimensional calibration. After the first reconstruction image was obtained, the lattice spacing was measured and compared to the values from TEM images and calculations. If it does not match with these values, a new image is reconstructed with some adjustments.

The dimensions of the 3D images can be affected by lots of factors such as microscope detection efficiency, accuracy of evaporation field value and estimates of tip geometrical shape. The first two can be well defined in the stage of instrument calibrations. For the last factor, the ultimate approach would be using TEM images to estimate the shape of the small analyzable volume. Since only 2D information can be obtained from TEM images and the procedure becomes much more time consuming and tedious, some other alternatives are more practical and gives good enough results. The tip radius can be estimated by the relationship:

\[ r = \frac{V_{\text{dc}}}{k \cdot F_e} \]  \hspace{1cm} (2-4)

Here the field potential for pure palladium is known as 37 V/nm. The initial voltage can be obtained from the voltage history graph (Fig. 2.9a) and the mass history graph (Fig.
2.9b). The voltage corresponding to the first appearance of predominant Pd peaks can be used to calculate the tip end radius. For the pure substance, the shape of voltage curve in the voltage history graph is a similar image of the shank shape of the tip according to (2-3) since k and F are constant thus r is proportional to $V_{DC}$. By carefully adjusting the initial tip radius and shank angles, the dimension of the 3D images can be brought close to reality. Figure 2.13d shows reconstructed image of a palladium tip. Lattice spacing was observed in the magnified region about 0.2 ~ 0.25 nm, which was consistent with the values from TEM images. From the reconstructed image, fcc planes were found perpendicular to the axial direction of the tip, which was also confirmed in TEM images.

The results of reconstruction images demonstrate the unparallel ability of atom probe microscope in three-dimensional analysis. The mass resolution down to single atom level enables the technique to analysis trace amount of solutes in the bulk materials and nanoscale buried features. But this ability has not been extended to lots of insulating materials because it’s not easy to prepare a perfect tip as the Pd tip shown here. Fortunately new sample configurations can be invented based on the mature metal tips. For example, monolayer formed on metal tips surfaces by specific chemical bonds will be able to be analyzed by the atom probe microscope. Variety of coating and depositing techniques can be used to construct variety of organic, polymeric and even biological thin films or composite films on
well defined metal tip surfaces for analysis under laser assisted surface evaporation. In the following chapters, new sample configurations will be developed according to the properties of the analytes for atom probe analysis. Three dimensional images will be obtained with a local electrode atom probe microscope for the first time. The work is aimed to make contributions to extending the technique application to fundamentally new areas.

2.6 References


(31) Seidman, D. N.; Sudbrack, C. K.; Yoon, K. E. The use of 3-D atom-probe


CHAPTER 3: ATOM PROBE TOMOGRAPHY OF MONOLAYERS

3.1 Introduction

Selective control of the chemical and physical properties in the surfaces is an
important subject in surface science and engineering. The technique is widely used in
surface protections\textsuperscript{1-7}, surface functionalizations\textsuperscript{8-13}, pattern constructions\textsuperscript{14-19} and
improvements in specific properties such as wetting\textsuperscript{20-22}, adhesion\textsuperscript{21,23-25}, lubrication\textsuperscript{26-28} or
biocompatibility\textsuperscript{29}. Direct imaging of the surface monolayers and sequentially attached
groups in nanoscale is of great interest in understanding the surface structures and
morphologies.

Three dimensional atom probe microscopy is a powerful technique for material
analysis because of its unparallel ability for providing both structural and compositional
information on nanoscales. The unique advantages of the technique include the single-atom
sensitivity and its better than 0.3 nm spatial resolutions in all three coordinates. For bulk
material analysis, the compositional sensitivity can be 10 appm or better\textsuperscript{30}. Recent
progresses have been made on the instrumentations greatly extend the applications of the
technique to analysis not only metallic and electrically conductive materials but also
insulating materials such as organic molecules. These features make the three dimensional
atom probe microscope an excellent tool for analyzing variety of monolayers. However
most of the current work has been focusing on subsurface and buried microstructures and no research has been done on any kind of monolayer analysis. In the present work, we will apply the atom probe tomography analysis on oxide, ionic and alkanethiol monolayers on metal surfaces.

**Figure 3.1.** Schematic diagram of the three dimensional imaging on variety of monolayers coated on the metal tips by an atom probe microscope.

The schematic diagram in **figure 3.1** explains the atom probe analysis processes. A variety of the monolayers will be constructed on the apex regions of conventional metal tips, including surface oxides, halogen ions and a thiol monolayer. The monolayers are chosen because of their important application in surface protections, surface
functionalizations and pattern constructions, also their ease to prepare as model systems for analysis. And no similar study on these has been done with APT technique. In the analysis the surface evaporation stimulated by external pulses takes place with precise control so that the surface atoms can be removed one at a time. The charged atoms pass through the hole in the counter electrode and are analyzed by sequentially a mass spectrometer and a position-sensitive detector. The positions and chemical identities of the atoms are used to restore the three dimensional image of the analyzed volume. The 3D reconstructed images will present both of the structural and compositional information of the near surface regions. The results are expected to identify the coated monolayers, to show the surface morphology of the monolayers, the interfaces with the metal substrates and estimated dimensions. This study is the first attempt to apply atom probe tomography technique on monolayer analysis.

3.2 Experimental Section:

3.2.1 Material and Reagents

Acetic acid (Fisher, glacial), absolute ethanol, perchloric acid HClO₄(Fisher, 70%), HCl (Fisher, ACS plus), HNO₃ (Mallinckrodt, 70%), potassium bromide KBr (Aldrich, a.c.s. reagent), potassium chloride KCl (Sigma, 99.0%), potassium iodide KI (Sigma, 99.0%), 1-hexanethiol CH₃(CH₂)₅SH (Aldrich, 95%, 234192) were used as received. Gold wire (0.20 mm, 99.999%) was purchased from Ernest Fullam (Latham, NY) for atom probe tip
preparation. 10 mM KBr, KCl and KI solutions were prepared respectively by dissolving the corresponding salts in 18 MΩ cm deionized water (NANOPure, Barnstead, Dubuque, IA). 10 mM thiol solution was prepared by mixing/dissolving the corresponding thiols in absolute ethanol. 10 mM HClO$_4$ solution was made by mixing HClO$_4$ with deionized water. These solutions will be used for monolayer constructions on the gold tips. The electropolishing fluid used to prepare needlelike tips was aqua regia solution (3:1 HCl and HNO$_3$).

3.2.2 Gold tip preparation.

A similar tip preparation as the electropolishing of Pd tips in chapter 2 was performed here for gold tip preparations. A brief description on the procedure is explained here. Typically two atom probe specimens were made from a piece of 10 mm long gold wire (0.2 mm diameter) in each electro-polishing process. The electropolishing fluid used to prepare atom probe tips was aqua regia solution (3:1 HCl and HNO$_3$). The wire was etched gradually with the polishing fluid in a Pt ring electrode under DC voltage of 4 V. A neck region formed and became thinner until being fractured by its own weight. The gold tips were then rinsed through deionized water, methanol and acetone, and then stored in vacuum for further treatments. To clean the tip surface, gold tips were pre-evaporated in the atom probe microscope before monolayer constructions.
3.2.3 Formation of thin films.

To create a thin oxide layer on the gold surface, the specimen was treated with oxygen plasma for 5 minutes at room temperature. The ionic monolayers were prepared by dipping the gold tips in 10 mM KBr, KCl or KI solutions for 10 minutes. Then the tips were immersed in 10 mM HClO$_4$ for 5 more minutes and rinsed by deionized water to remove physisorbed ions. To construct the thiols monolayers, the gold tips were mounted on homemade Teflon holders and immersed in the thiol solution for 10 minutes. Then the tips were rinsed by pure ethanol to removed physisorbed molecules. All coated gold tips were immediately transferred into the buffer chamber for degassing before atom probe analysis.

3.2.4 Atom probe microscopy.

The specimens with treatments were analyzed by atom probe microscope with laser pulsing. Briefly a standing voltage $V_{DC}$ was applied on the local electrode to create the potential field close to the level for field evaporation (usually 10 ~ 50 V/nm). Ultrafast laser pulses were focused on the tip surfaces to stimulate the surface evaporation. The laser pulse frequency used was 250 kHz. During analysis, $V_{DC}$ was ramped up gradually to maintain constant evaporation rate along with proper laser pulse energy. The evaporated ions passed through the time of flight mass spectrometer before the position-sensitive detector. The chemical identity of each ion and its position on the X-Y coordinates of the detector plate was then detected. The IVAS software (Imago) was used for post reconstruction of the 3D
image of evaporated volume and consecutive analysis. Briefly when the surface of a coated tip was peeled off atom by atom in surface evaporation, the lateral position of individual ion was recorded along with its mass to charge ratio. After a series of ions were detected and recorded in each pulse, a sequence of hit records was obtained in the test. The sequence composed of millions of hitting records was used to reconstruct the 3D image of the evaporated volume. The X-Y positions in the record were used to identify the original locations of the atoms in a layer. The sequence of hitting atoms was used to locate the atoms in the specific layer which corresponds to its position in depth direction, and to identify the order of layers as well. The types of atoms were determined as mentioned in previous paragraph and coded according to their chemical identities. Thousands of two dimensional slices were then used to construct the three dimensional image.

3.3 Results and Discussion

3.3.1 Surface cleaning.

Before coating monolayers on the gold surfaces, it’s important to know the prior surface conditions of the tips. An optical image of a fresh made gold tip is shown in figure 3.2.
A clean surface is necessary for monolayers to form on. Therefore pre-evaporation in the atom probe microscope is the best approach to clean the tip surfaces. On the other hand, protruding area on the tip surface needs to be removed. The potential field in protruding areas can be greatly enhanced due to the smaller curvatures, which will cause preferential evaporation. Preferential evaporation will alter the evaporation sequence. As mentioned in chapter 2, this will bring difficulties in the consecutive image reconstruction. In order to smooth the surface and clean the adsorbates, a few layers of surface atoms on fresh made gold tips were evaporated in the atom probe microscope before coating the monolayers. The mass spectrums obtained before and after surface cleaning steps show the difference in the surface composition. The two mass spectrums are given in figure 3.3a and b.

From the comparison of the two mass spectrums the fresh made surface was found having several types of adsorbed molecules which does not appear in the mass spectrum for
Figure 3.3. Mass spectrums obtained from the surfaces before (a) and after (b) the surface clean step. The adsorbates on the surface of the fresh made gold tip include $O^+$, $H_2O^+$, $CO^+$, $CO_2^+$ and $SO_2^+$ ions as shown in (a). After evaporation of several layers of surface atoms, the amount of adsorbates was significantly reduced (b). The pre-evaporated surface. Peaks at 16, 28 and 44 in figure 3.3a correspond to $O^+$, $CO^+$ and $CO_2^+$ respectively. Peaks at 18, 64 are the ions of $H_2O^+$ and $SO_2^+$. These peaks does not appear in the mass spectrum from the surface after pre-evaporation (in figure 3.3b). Because of the small tip end radius $< 100$ nm and its hemisphere shape, lots of steps and kinks exist in the tip apex. Therefore the surface tends to adsorb more molecules than flat surfaces. The
peaks found at 98.5 and 197 in both mass spectrums correspond to Au$^{2+}$ and Au$^+$ ions respectively from the gold surface.

The mass spectrum analysis shows that the apex region of gold tips can be effectively cleaned by pre-evaporation in the atom probe microscope which follows the similar operation as atom probe imaging. Several species were found as residuals on the fresh-polished gold tip including water molecules, carbon dioxides, sulfur dioxides and oxygen gas molecules. After cleaning the surface was free of adsorbates and ready to be used for monolayer formations.

### 3.3.2 Oxide layer on gold surface formed by oxygen plasma treatments

Oxidation of the polycrystalline gold surface has been studied for the purposes of surface functionalizations$^{31}$ and catalyst developments$^{32-38}$. Oxygen activated by high frequency discharge has been suggested to form the oxide layer on the gold surface$^{39,40}$. Some results show that the exposure to oxygen plasma produces gold oxide Au$_2$O$_3$ which are distinguished from physisorbed O$_2$ molecules evidenced by binding energy shifts$^{41,42}$. The atom probe microscope can be used to reveal the surface composition of the gold treated by oxidation with its single-atom sensitivity. The mass spectrum analysis can be expected to provide useful information to distinguish the surface oxides from physisorbed O$_2$ molecules. The three-dimensional image of the surface layer can be also reconstructed.

The fresh-polished gold tip as shown in figure 3.2 was cleaned by pre-evaporation with laser pulsing to remove the residuals. Mass spectrum from the surface before cleaning
Fig. 3.3a) shows O⁺, Au²⁺ and Au⁺ ions. After cleaning, the resulting mass spectrum (Fig. 3.3b) only shows Au²⁺ and Au⁺ ions which are evaporated directly from the gold substrate. After the surface cleaning, the gold tip was treated with O₂ plasma at the room temperature. Different durations of plasma treatments were tried and it was found that treatments longer than 5 minutes were enough for forming oxide layers on the gold surfaces. After treatments the gold tip was transferred into the atom probe microscope immediately and stored in vacuum at room temperature for 6 hours for degassing. In the atom probe analysis, the gold tip was cooled to a cryo temperature to minimize the thermal noise in surface evaporation. The stable surface evaporation was carried out assisted by laser pulsing similar as in pre-evaporation cleaning. The resulting mass spectrum for the test is given in figure 3.4 with full range and a range focused in low mass-to-charge region.

Similar to the mass spectrum from the pre-cleaned gold surface, Au²⁺ and Au⁺ peaks were found after the O₂ plasma treatment. Besides these, additional peaks were also found corresponding to AuO⁺ (213 m/u) and AuO₂⁺ (229 m/u) and those in the low mass regions including N⁺, O⁺, H₂O⁺, H₃O⁺, NO⁺, O₂⁺, CO₂⁺ and NO₂⁺. The AuO⁺ and AuO₂⁺ ions does not appear in the mass spectrums from either pre-cleaned surface or fresh-made surface, therefore they should be evaporated directly from the gold oxide layer. The mass spectrum in the low mass region shows variety of O and N related peaks which were not found from the pre-cleaned surface either. After the plasma treatment, the surface became more hydrophilic. The H₂O⁺, H₃O⁺ comes from the water vapor adsorbed in the sample transfer. Although the
Figure 3.4. The mass spectrum obtained from an $O_2$-plasma treated gold tip. The full range mass spectrum is given in (a) and a shorter range focused in low mass-to-charge region is in (b). Ions of $AuO^+$ and $AuO_2^+$ were found which were not presented in the mass spectrum of fresh-polished tip. $Au^{2+}$ also appears. In the low mass range, variety of ions were detected including $N^+$, $O^+$, $H_2O^+$, $H_3O^+$, $NO^+$, $O_2^+$, $CO_2^+$ and $NO_2^+$. These ions were not detected on the pre-cleaned gold surface.

gold tip was degassed for several hours at room temperature, the water molecules were not eliminated completely. In the plasma treatment, low partial pressure air was acted as the
oxygen source for gold oxidation. Therefore the N containing species detected in the mass spectrum were formed on the surface during the treatment.

The three dimensional image of the surface region were reconstructed from the data acquired in the surface evaporation. The 3D iso-concentration surfaces and 1D atomic concentration distributions are presented in figure 3.5a & b. The iso-concentration surfaces are used to find the interface and define the boundaries of bulk phases. As shown in Fig. 3.5a, the oxide layer is enclosed in the red surface on the top of the yellow surface which defines the gold substrate. The 3D image gives an insight view of the subsurface composition profiles in a 30 nm × 30 nm × 30 nm volume.

Figure 3.5. Atom probe analysis of gold oxide layer formed by oxygen plasma treatment. The iso-concentration surfaces for gold oxide AuOₓ and gold subsurface region Au were constructed in (a). The yellow surface refers to the Au substrate. The red surface refers to the oxide layer. The concentration distributions along the depth from the initial surface for Au and O are shown in (b).
A more detailed compositional analysis was performed along the depth direction as shown in Fig. 3.5b. The 1D atomic concentration distributions were constructed by calculating the concentration of specific species over the slices of horizontal cross-sections along the depth direction. The Au and O atomic concentrations were computed respectively. The thickness of the oxides layer estimated from the chart is about 10 nm, which is close to the reported values from oxygen plasma oxidized gold surfaces. The Au:O ratio in the topmost 2 nm region is close to 2:3 suggesting the oxides on the surface are Au$_2$O$_3$, which is consistent to the results from other reports$^{41,42}$. With increasing depth, this ratio becomes close to 1:1, suggesting the oxides in the deeper region were mainly AuO. The O content keeps decreasing along the depth and eventually decreases to less than 1% at 22 nm beneath the surface.

The atom probe tomography on the oxygen plasma treated gold surface proves that the Au$_2$O$_3$ was formed on the surface. The thickness of the oxide layer was measured to be about 10 nm. The analysis provides direct observation of the nanoscale surface morphology which is usually a nontrivial job by other methods such as XPS or Auger electron spectroscopy.

### 3.3.3 Ionic monolayers

As mentioned in the introduction section, monolayer construction is widely used in surface protections, surface functionalizations and pattern constructions. Halogen elements
have been used to form the monolayer on metal surfaces for variety of purposes\textsuperscript{44,45}. Direct imaging of monolayers has been performed on flat metal surfaces by STM\textsuperscript{46-49}. However the monolayers formed on irregular surfaces such as on nanoparticles are hard to be resolved by conventional approaches. In this section, the atom probe microscope will be used to visualize the monolayers of Cl, Br and I atoms covered on the surfaces of gold atom probe tips with <100 nm diameter. The ionic monolayers were constructed on pre-cleaned gold surfaces by dipping the tips in diluted salt solutions. The physisorbed species were rinsed off the surfaces. Similar procedures were performed as in the previous atom probe analysis on oxide layers.

The mass spectrums from three monolayers are given in figure 3.6. In all the analysis the surfaces were evaporated until the clean gold surfaces were reached. Au\textsuperscript{+} and Au\textsuperscript{2+} peaks appear in all the mass spectrums. The mass spectrum in Fig. 3.6a was obtained from the Cl monolayer. Clear Cl isotopic peaks from the two isotones \textsuperscript{35}Cl and \textsuperscript{37}Cl were detected. Another set of peaks at 36 and 38 u/e were also found which are corresponding to the hydrogen chloride molecules of the two isotones. An inserted mass spectrum in Fig. 3.6a shows the low mass region (1~50 u/e). The residuals found in the surface are H\textsubscript{2}O and CO\textsubscript{2} which came from the solution. Same residuals also appear in Br and I covered surfaces. The mass spectrum from the Br covered gold surface is given in Fig. 3.6b. Besides clear Au\textsuperscript{+} and Au\textsuperscript{2+} peaks, the \textsuperscript{79}Br and \textsuperscript{81}Br isotones were also detected in the forms of single charged and double charged ions. The \textsuperscript{79}Br\textsuperscript{+} and \textsuperscript{81}Br\textsuperscript{+} appear at the mass-to-charge ratios of 79 and 81. The \textsuperscript{79}Br\textsuperscript{2+} and \textsuperscript{81}Br\textsuperscript{2+} can be found at 39.5 and 40.5. The mass spectrum from the I covered
Figure 3.6. The mass spectrums from ionic monolayer covered gold surfaces. The monolayers were constructed on the pre-cleaned gold surfaces by (a) Cl, (b) Br and (c) I ions from their diluted salt solutions. The mass spectrums show corresponding peaks of Cl$^+$, HCl$^+$ in (a), Br$^+$ and Br$^{2+}$ in (b) and I$^-$, I$^{2+}$ in (c) and Au$^+$ and Au$^{2+}$ from the gold substrates.
gold surface is presented in Fig. 3.6c. Single and double charged I ions were found at 127 and 63.5 respectively. There is no Au-containing ions appears in the all three types of surfaces. All the mass spectrums show the existence of adsorbed ions. Since the surfaces were rinsing for several times before the analysis, the physisorbed ions should be removed efficiently. Therefore from the results the monolayers of halogen ions were successfully constructed on the apex of needlelike gold atom probe tips.

The three dimensional images were reconstructed for the three types of monolayers respectively and are presented in figure 3.7. The isoconcentration surfaces of Cl in (a), Br in (c), I in (e) and gold substrates (blue) were constructed to find the ion enriched regions. The 3D dot images of magnified volumes across the monolayer-gold surface interfaces from the three samples, Cl-Au in (b), Br-Au in (d) and I-Au in (f) were reconstructed to show the atoms spatial distributions. In figure (a), (c) and (d), the halogen ion enriched regions all appear on the top of gold substrates, suggesting that the ions covered the apex regions of the gold tips. Distinct interfaces appear between the monolayers and gold surfaces, which are consistent with the information from the mass spectrums that no complex ions such as Cl-Au, Br-Au and I-Au was detected. The detailed nanoscale structures near the interfaces are presented in the dot images in figure (b), (d) and (f). The Cl, Br and I ions all were detected in the first 1 ~ 2 nm deep regions from the initial surfaces. These images provide direct observations of the existence of the ionic monolayers.
Figure 3.7. 3D isosurfaces and dot images of the ionic monolayers on the gold surfaces. Images of three types of monolayers including Cl (a and b), Br (c and d) and I (e and f) are given the figures respectively. The black bars represent the scale of 5 nm.

The one dimensional concentration distributions of adsorbed ions and gold atoms are given in figure 3.8. From the charts the thicknesses of monolayers can be directly found.
Figure 3.8. 1D concentration distributions from the monolayer analysis. The monolayer concentrations of Cl (a), Br (b) and I (c), and gold substrates were calculated along the depth direction from the tip initial surfaces.
The Cl monolayer is estimated about 0.5 nm thick, Br monolayer about 0.8 nm and I monolayer about 1 nm. It is necessary to mention that thickness of the monolayers read directly from the 1D concentration profiles are also affected by the surface roughness and the orientation of the monolayer-gold substrate interfaces. The concentration at specific depth is averaged over the cross-sectional plane perpendicular to the depth directions. If the monolayer-metal interface is perfectly smooth, and parallel to the depth direction, the true lateral concentration can be obtained. Therefore the thickness of the monolayers obtained here are a little greater than the true values.

In this section, the ionic monolayers on the gold surfaces were successfully analyzed by the atom probe microscope. The monolayers were directly constructed on pre-cleaned needlelike gold tips. Trace amount of adsorbed Cl, Br and I ions were detected by the mass spectrometer. The spatial distributions of the ions were resolved after the 3D images were reconstructed. The isoconcentration surfaces of Cl, Br and I enriched layers were found all covering on the top of gold substrates. The monolayers on the gold surfaces were then successfully visualized. The thicknesses of the monolayers were read from the 1D concentration distributions, which are close to the reported values. The results prove that the atom probe tomography is a powerful technique to analyze the single-atom monolayers.
3.3.4 Alkanethiol monolayers

Thiol-gold monolayers play very important roles in surface protections, surface modifications, pattern constructions and improvements in specific properties such as wetting, adhesion, lubrication or biocompatibility as mentioned before. Most of current analysis approaches are to get averaged signals over finite areas which decrease the resolution in some directions. With the increasing demands in the surface modifications, the features of interest become smaller and reach to nanoscale. More complex structures have been developed such as multilayers, microelectronics with 3D structures and biomolecules grafted on the monolayers. The atom probe microscope is potentially the most suitable tool for analyzing such systems. Here we report the first analysis of thiol grafted gold surfaces by 3D atom probe tomography.

Monolayer of 1-hexanethiol (CH$_3$(CH$_2$)$_5$CH$_2$SH) (molecule weight:118.24) was prepared on the gold tip. Similar to the previous monolayer construction, the thiol is directly attached onto the apex of the needlelike gold tips after pre surface cleaning. Given enough time for the monolayer formation in the solution, well packed thiol layer can be obtained as shown in figure 3.9.
Figure 3.9. Schematic structures of a 1-hexanethiol molecule and the monolayer on the gold surface.

Since the organic layers are insulating materials which can significantly reduce the near surface potential strength and alter distribution for field evaporation, voltage pulsing is not suitable for the surface evaporation. Instead the laser pulse was used in the examinations to assist the surface evaporation of the thiol monolayer. The resulting mass spectrum from the coated gold tip is given in figure 3.10.

In the mass spectrum, Au\(^+\) and Au\(^{2+}\) ions appear as from the evaporation of the gold substrate. In the low mass regions, groups of peaks can be found whose mass-to-charge ratios are consistent with the weights of fragment ions from the breakage of the thiol molecules. The evaporation was carried out with the standing voltage \( V_{DC} \) ramping up in the range of 2000 – 8000 V. The field strength near the gold tip surface is estimated about 10 ~ 40 V/nm, which is high enough to cause fragmentation of the organic chains.
Figure 3.10. Mass spectrum of the 1-hexanethiol covered gold atom probe tip. The full range spectrum is given in (a). Several regions corresponding to different fragments are put into separated spectrums (b ~ e) for peak identifications.
From peak analysis in Fig. 3.10b, the fragments of thiols found are listed in Table 3.1.

The linear alkane chains of the thiols can be broken into shorted fragments in the form of $C_nH_{2n}$. Under the high positive potential field fragments can lose one or more hydrogen atoms and form lighter ions $C_nH_x$.

**Table 3.1. The fragments from the surface evaporation of the hexanethiol layer.**

<table>
<thead>
<tr>
<th>$m/n$</th>
<th>Fragment</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 - 15</td>
<td>$CH_x$</td>
</tr>
<tr>
<td>24 - 29</td>
<td>$C_2H_x$</td>
</tr>
<tr>
<td>36 - 43</td>
<td>$C_3H_x$</td>
</tr>
<tr>
<td>44 - 46</td>
<td>$C_3H_x$ &amp; $S(CH_x)$</td>
</tr>
<tr>
<td>55 - 58</td>
<td>$C_4H_x$ &amp; $S(C_2H_x)$</td>
</tr>
<tr>
<td>72 - 85</td>
<td>$(CH_2)_5CH_3$</td>
</tr>
<tr>
<td>115 - 118</td>
<td>$S(CH_2)_5CH_3$</td>
</tr>
</tbody>
</table>

The sulfur containing fragments were also found. The single hexanethiol molecules, $S(CH_2)_5CH_3^+$, were founded at the mass-to-charge ratios in 115 ~ 118 u/e. The molecular weight of the thiol is 118.24. The molecules can lose several hydrogen atoms and form lighter ions with 1~3 less mass-to-charge ratios than the original ions. In the high mass region (d), Au containing ions were found including $Au(H_2O)^+$, $Au(CO)^+$, $AuS^+$ and $Au(H_2O)_2^+$. The Au- $S(CH_2)_5CH_3^+$ also appears at 315 u/e as shown in (e).

After the mass spectrum analysis, the detected ions were assigned to different chemical identities. Then all the ions were used to construct the 3D images according to their lateral positions detected by the position-sensitive detector and in the evaporation sequence. The images are illustrated in figure 3.11.
Figure 3.11. 3D images of the hexanethiol covered gold surface. The dot image containing the ions identified in the mass spectrum analysis is presented in (a). The atomic isoconcentration surfaces for carbon, sulfur and gold atoms were constructed as in (b). The black bars refer the scale of 1 nm.

The 3D dot image in (a) are constructed with all ions identified in Fig. 3.11. The gold substrate (blue region in Fig. 3.11a) is covered by a mix layer of organic fragments and other ions including water molecules. In order to identify the thiol layer, the ions was decomposed into elements to construct atomic isoconcentration surfaces for carbon, sulfur and gold atoms as shown in Fig. 3.11b. Since the carbon and sulfur atoms are only from the thiol molecules, their spatial distribution provides the information about the location of thiols. The sulfur isosurfaces (yellow) are located on the top of the gold substrate (blue). They are embedded in the carbon isosurface which encloses most of the volume of the mixed layer found in Fig. 3.11a. The element distributions are consistent with the structure of thiol monolayer on gold substrate in Fig. 3.9.
1D atomic concentration profiles was used to identify the layer composition as shown in Figure 3.12. In order to construct the 1D concentration distributions, the ions were decomposed into individual atoms which were used to compute the new elemental concentrations. The contents of C, H and S decrease drastically in the region of 2 to 2.3 nm deep from the surface, where the Au content gradually increases to over 95%. The covered layer in the first 2 nm was composed of organic molecules. The ratio of C, H and S concentrations keeps almost constant in the layer. The stoichiometry of it is calculated to be $C_6H_{13.4}S$, which is consistent with the composition of hexanethiol ions $C_6H_{15}S^-$.

Figure 3.12. 1D atomic concentration distributions of C, S and H along the depth obtained from the analysis of the hexanethiol covered gold surface. The thickness of the thiol layer is about 10 nm. The detected stoichiometry of the top layer is $C_6H_{13.4}S$ which is consistent with the composition of hexanethiol molecules.

The monolayer thickness of hexanethiol on metal surface has been reported approximately 0.6 ~ 0.8 nm$^{50}$, which is thinner than the thickness estimated from the atom probe 3D reconstruction. The discrepancy may be due to the overestimated thickness by
current algorithm used in the APT data analysis, which is based on single component material model. The metal substrates are normally used to estimate the dimensions based on the pure metal evaporation field $F_{metal}$. But for the thiol monolayer coated metal tip, the evaporation fields can be significantly different in the two phases. The data base of $F_{metal}$ is available in literatures, but there is no data for variety of nonmetallic materials. Therefore, the 3D images of coated tips are reconstructed based on the $F_{metal}$, which causes inaccurate dimension estimations on the monolayers. Because of the small thickness of monolayer, the evaporation of the organic layer is fast. Therefore the $F_{thiol}$ is hard to estimate accurately from the evaporation voltage history. In the next chapter, we will introduce a field strength correction after image reconstruction on thicker polymer layers from which $F_{polymer}$ can be estimated from voltage history.

In this section, a hexanethiol covered gold surface was successfully analyzed by the atom probe microscope. The thiol layers were directly constructed on pre-cleaned needlelike gold tips. Fragmentation of the thiol molecules in the surface evaporation were detected by the mass spectrometer. The 1D distributions of C, H and S were obtained to determine the stoichiometry of the coating layers. The resulting composition $C_6H_{13.4}S$ of the organic layer was consistent with hexanethiol molecules. Thickness of the thiol layer was found about 2 nm. The results prove that the atom probe tomography is a suitable technique to analyze ultrathin organic layers on metal substrates.
3.4 Conclusions

In this chapter, variety of thin surface layers including oxides, ionic monolayer and thiol layers constructed on the needlelike gold atom probe tips were prepared and analyzed using the atom probe microscope. Formation of thin gold oxide layers by oxygen plasma treatments was confirmed by mass spectrum analysis and atomic concentration distributions. The 1D concentration analysis of the oxide layers suggested that the oxides near the surface were $\text{Au}_2\text{O}_3$, and then $\text{AuO}$ became predominant. In ionic monolayer analysis, the trace amount of adsorbed Cl, Br and I ions were detected by the mass spectrometer. The isoconcentration surfaces of Cl, Br and I enriched layers were found all covering on the top of gold substrates. The monolayers on the gold surfaces were then successfully visualized. The thicknesses of the monolayers were read from the 1D concentration distributions, which are close to the reported values. In the thiol layer analysis, molecule fragmentation was observed from the corresponding mass spectrum analysis. The composition of the organic layers detected in the 3D reconstruction images was determined to be $\text{C}_6\text{H}_{13.4}\text{S}$ by atomic concentration distributions, which was consistent with the stoichiometry hexanethiol molecules ($\text{C}_6\text{H}_{15}\text{S}$). The results demonstrate that the atom probe tomography is a powerful technique to analyze the monolayers.

In 3D image reconstruction, the current algorithm for dimension estimation is based on single component material model. The metal substrates are normally used to estimate the
dimensions based on the pure metal evaporation field $F_{\text{metal}}$. This is an effective and simple approach for single phase material. But for monolayer coated tips, especially by organic monolayers, the evaporation fields can be significantly different in the two phases. Although the data base of $F_{\text{metal}}$ is available in literatures, but there is no data for variety of nonmetallic materials. Because of these reasons, the 3D images of coated tips are reconstructed based on the $F_{\text{metal}}$, which causes inaccurate dimension estimations on the monolayers. In the next chapter, we will introduce a field strength correction after image reconstruction on thicker polymer layers from which $F_{\text{polymer}}$ can be estimated from voltage history.

3.5 References


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CHAPTER 4. ATOM PROBE TOMOGRAPHY OF ELECTRODEPOSITED POLYMERS

4.1 Introduction

Atom probe tomography has been used extensively to acquire information about metallic materials and semiconductors\textsuperscript{1,2}, but its applications to macromolecules and polymers have been limited due to difficulties to evaporate insulating materials and lack of appropriate sample preparation methods\textsuperscript{2}. In early studies, a few biomaterials such as ferritins and nucleic-acids were imaged by FIM\textsuperscript{3-5}, but no three dimensional analysis has been achieved so far. Several other studies on organic materials including polypyrrole\textsuperscript{6} and phthalocyanine\textsuperscript{7} provided only limited information in mass spectrum, without successful image reconstruction on the analyzed volumes. For example, Maruyama et al. reported the first atom probe analysis on polypyrrole and polystyrene\textsuperscript{7}, which were deposited on tungsten tips. The mass spectrum from the low field region showed monomer, dimer, trimer and fragments, while tungsten evaporation was found in the mass spectrum from the high field region. In their work, no further investigation was provided except for the mass spectrum analysis. The difficulties of analyzing these materials include sample preparation, data interpretation and experiment optimization. Because conventional atom probe analysis utilizes field evaporation under high electrical fields to remove surface atoms, the materials for tests are expected to be electrically conductive to pass the externally imposed voltage to...
the end of the sharp atom probe tips. Although the conducting polymers possess the electrical conductivity up to 100 S/cm, that is still several orders of magnitude lower than metals, which was the major obstacle preventing the utilization of atom probe tomography from analyzing these materials. With the introduction of laser induced ionization to the atom probe microscopy, it becomes possible to analyze insulating materials such as organics, polymers and biomaterials. Another difficulty is to interpret the evaporated ions detected by the mass spectrometer. Ionization of polymers is different from metals, since the detected ions are not only individual atom but also polymer fragments and molecule ions. Since the ionization is carried out under high electrical potential and laser pulse energy, fragmentation of polymers is expected to be more severe than that in common mass spectrum analysis. In Maruyama’s reports on polypyrrole and polystyrene, variety of polymer fragmentations are observable in mass spectrums but no further investigation has been done to interpret the pattern of mass-to-charge peaks. The latest commercial atom probe microscope enables adjustments on laser pulse energy levels, which can be used to probe the effects of operation parameters on mass spectrum pattern and to help data interpretation. On the other hand, applying this technique to new materials is very important not only to expand this unique technique’s ability, but also to accelerate and deepen the understanding on many novel material systems which can not be well defined by most of current techniques.

In this report, our investigation will focus on polymers that may be electrodeposited from their monomer solutions, including conducting polymers and insulating polymers.
Electrodeposited polymers have attracted interests for potential application in electroluminescence\(^8\)\(^-\)\(^10\), electro catalysis\(^11\)\(^-\)\(^14\), separation\(^15\)\(^,\)\(^16\), biosensors\(^17\)\(^-\)\(^20\), energy conversion and storage\(^21\)\(^-\)\(^24\) and corrosion protections\(^25\)\(^-\)\(^28\). We chose these polymers for analysis because they can be deposited onto conductive surfaces with complex geometric shapes, especially at the end of the atom probe tips whose diameter is typical less than 100 nm. The formation of polyaniline (PANi) and polyphenol (PPO) as examples are demonstrated in Equation (4 - 1) and (4 - 2) respectively\(^29\).

\[
\text{Aniline electropolymerization:} \\
\text{Phenol electropolymerization:}
\]

The monomers can be electropolymerized from aqueous solutions under external potentials. The resulting polymers are able to deposit on conductive surfaces as thin films. Polyaniline (PANi) is a conducting polymer which possesses an electrical conductivity up to 100 S/cm. There are other conducting polymers such as polypyrrole and polythiophene. Polyphenol (PPO) is an insulating polymer, which forms thinner films due to its self-limiting growth. Its derivatives such as poly(aminophenol) (PAPO) can be also electrodeposited.

They are widely used to modify surfaces and to trap biomolecules for sensor developments\(^30\)\(^-\)\(^33\).
Based on the ability to be directly electrodeposited onto conductive surfaces, a new configuration of atom probe sample for polymer analysis is proposed in this report: a thin layer of polymer electrodeposited onto a pre-sharpened atom probe tip. Compared to polymer tips sharpened from bulk materials or thin films, this method has several advantages. First, it simplifies sample preparation. Electrodeposited films can be adjusted easily by control of the deposition. Secondly, the metal tips can be made by conventional preparation methods such as electropolishing. Their shapes can be accurately adjusted by tuning the polishing parameters and pre-evaporation in atom probe microscope. In this design, the metal tip surfaces function as the conducting substrates for polymer deposition. If uniform polymer coatings are retained, the polymer layer will inherit the shape of the metal substrate, therefore avoid further reshaping. Thirdly, this sample configuration significantly enhances the local field strength on polymeric materials comparing to the tips made from pure polymers since polymer layers on metal tips are much thinner. Therefore highly conductive metal substrates are able to deliver majority of the imposed voltage on the thin polymer layers for ionization. Most importantly, numerous researches have shown that electropolymerizable polymers are able to encapsulate variety of very important sub micron systems such as nanoparticles, macromolecules, proteins, enzymes and other biomaterials. The merit of the polymers enables this sample design for wide applications in further developments such as construction of polymer encapsulated nanoparticles or macromolecules for atom probe analysis.
In this report, we present the implementation of a novel sample design for polymeric material analysis by atom probe microscopy. Several polymers electrodeposited on sharp metal tips will be investigated, including conducting polymers such as polyaniline, polypyrrole and polythiophene, and insulating polymers such as polyphenol and poly(3-aminophenol). The resulting polymer coatings and polymer-metal substrate interfaces will be analyzed and visualized by an atom probe microscope for the first time.

4.2 Experimental Section

4.2.1 Material and Reagents

Aniline (ACS reagent, ≥99.5%, Sigma-Aldrich), phenol (99.5%, Fluka) and chloroplatinic acid hydrate (99.9%), perchloric acid (70%, certified ACS, Fisher), glacial acetic acid (reagent ACS, Fisher) and concentrated sulfuric acid (Fisher) were used as received. Palladium wire (99.9%, 0.20 mm diameter) was acquired from Structure Probe, Inc./SPI Supplies (West Chester, PA). All solutions were prepared with 18 MΩ demonized water (18 MΩ NANOPure, Barnstead, Dubuque, IA) and were degassed by N2 gas purging for 10 minutes prior to use. Ultra-high purity N2 and He gases for LEAP analysis were obtained from Linweld (Des Moines, IA). Solution for polyaniline depositions was by adding proper amount of monomers into 100 ml 0.5 M H2SO4 aqueous solution. Solutions for polypyrrole and polythiophene depositions were by adding proper amount of monomers into 100 ml acetonitrile. The concentration of the monomers used for the three polymer
depositions were 40 mM. The monomers were dissolved by bubbling N\textsubscript{2} gas for 10 minutes. The solutions used for polyphenol and poly(3-aminophenol) deposition were made by adding 0.376 g phenol or 0.437 g aminophenol into 100 ml 0.1 M NaH\textsubscript{2}PO\textsubscript{4} solution. The crystals were dissolved by N\textsubscript{2} bubbling as well. The concentrations of monomers in both solutions were 40 mM. The pH’s of the solutions were adjusted to neutral with 1M NaOH.

4.2.2 Tip Preparation

Detailed tip preparation has been explained in chapter 2. A brief description on the procedure is given here. Typically two atom probe specimens were made from a piece of 10 mm long palladium wire (0.2 mm diameter) in each electro-polishing process. The wire was etched gradually with a Pt ring electrode in universal polishing fluid with DC voltage of 4 V. A neck region formed and became thinner until being fractured by its own weight. The specimens were subsequently rinsed through with water, methanol and acetone to remove surface contaminants. To achieve atomically smooth surfaces, Pd tips were pre-evaporated in the atom probe microscope before depositions.

4.2.3 Electrodeposition of Polymer

Polymer coatings on Pd tips were prepared by electrochemical polymerization of corresponding monomers in solutions with metal tips acting as working electrodes. Cyclic voltammetry was performed for electrodepositions via a potentiostat (CHI 760B, CH Instruments, Inc). A three-electrode electrochemical cell was used with an Ag/AgCl
reference electrode, a piece of Pt wire as counter electrode and metal tips as working electrode. The number of potential cycling and scan rate were adjusted to control the film thickness. The coating quality was checked by an optical microscope. Polyaniline coated tips were rinsed by 0.5 M H₂SO₄ for 3 times and 5 more potential cycles were applied in 0.5 M H₂SO₄ to remove monomer residues. After this, the film was rinsed by deionized water for 3 times and submerged in 50 °C deionized water for 3 hours to remove H₂SO₄. Polyphenol coated tips were rinsed by deionized water for 3 times. Coated tips for atom probe analysis were stored in the buffer chamber of the microscope under room temperature.

4.2.4 TEM Imaging

The polyphenol coating was characterized using a Tecnai G2 F20 scanning transmission electron microscope (STEM) at an accelerating voltage of 200 kV. Chemical composition of the deposited films was mapped with an energy dispersive x-ray detector. The coated tips were imaged after necessary cleaning. Tips were clipped on a standard sample holder with their sharp end being freely suspended in the hole to avoid damage from any contact.

4.2.5 Atom Probe Analysis

The polymer coated tips were analyzed by the atom probe microscope under laser mode. Standing voltage $V_{DC}$ was applied on the local electrode to create high potential field near the tip surface. Ultrafast pulse laser was superimposed on the specimens to stimulate
surface evaporation. The laser pulse frequency was 250 kHz. The laser pulse energy was adjustable in a range of 0.2 ~ 5 nJ. Flight length was set to 90 mm in order to detect the low energy fragments evaporated under lower voltage. During surface evaporation, $V_{DC}$ was ramped up gradually to maintain stable evaporation rate. The emitted ions passed through the TOF-MS before being detected by the position-sensitive detector. Chemical identities of ions and their trajectories detected by the position sensitive detector were recorded in a computer file. The experiments were stopped when enough hits collected from the metal substrates. Usually 2,000,000 atoms are appropriate to reconstruct the image for the substrates. All analysis including reconstructing 3D images from evaporated volume, finding isoconcentration surfaces and conducting concentration profiles were done with the IVAS software (purchased from Imago Inc).

4.3 Results and Discussion

4.3.1 Polyphenol analysis

Phenol and its derivatives have been used to form insulating polymer films < 100nm thick on conducting surfaces by electrodeposition\textsuperscript{18}. A variety of applications using polyphenol coatings has been reported for corrosion protection, electrode functionalization and protein imbilizaiton\textsuperscript{34-41}. Because of the low electrical conductivities of the forming layer, the film growth is self-limiting. This property makes the thickness of the polymer layer over an area very uniform. This type of polymers has been used to cover rough surfaces with
irregular shapes\textsuperscript{42}. Atom probe tips have very high surface curvatures in their region of interest, that is, the apex of the tip ends. It is found in our preliminary investigation that forming a uniform layer around the tip apex is difficult for lots of polymers. In figure 4.1a~f, coatings on metal tips by different types of electrodeposited polymers are inspected with an optical microscope. The polymers include conducting polymers such as (a) polypyrrole, (b) polythiophene and (c and d) polyaniline (PANI), and insulating polymers such as (e) polyphenol (PPO) and (f) poly(3-aminophenol) (PAPO). It can be found that all the conducting polymers tend to form overgrown thick layers on the metal tips. In fig. 4.1d, the PANi film was deposited with special treatments which will be introduced in later sections. The shape and thickness of the films are harder to control compared to the insulating polymers which follow the self-limiting growth mechanism. Because of the faster growth and thicker layers formed by conducting polymers, the thicknesses of the layers are not uniform over the apex region, and apex regions are barely covered by the polymers, as shown in (a) and (b). The surfaces of these coatings are also very rough. However, in atom probe analysis, only regions close to the tip ends can be effectively evaporated. Therefore, with the proposed sample design, our current work focuses on PPO and PAPO which can be easily coated on the sharp tips. With special deposition procedure, ultrathin PANi layers coated on metal surfaces can also be used for sample construction. These polymers will be very useful in the later research as encapsulating layer to trap nanoparticles.
Figure 4.1 Optical images of coated metal tips with electrodeposited polymers. Polypyrrole (a), polythiophene (b) and polyaniline (c) coatings are not able to form smooth layers and to fully cover the apex areas. The polyaniline deposited from very low monomer concentration (d) can form a thin layer on the sharp tip. The polyphenol (e) and poly(3-aminophenol) (f) can form ultrathin coatings on the metal surfaces, which can not be observed from the optical images. The presence of the PPO and PAPO films on surfaces will be observed later in the TEM images. The size of the images is 40 \( \mu m \times 30 \mu m \).
In this section, identifying and visualizing polyphenol coatings on metal surface by the atom probe microscope will be carried out for the first time. Investigation began with polymer electrodeposition on sharp palladium tips. Pd is chosen because it supports electrodeposition of PPO films under positive potential. Other metals such as Al would form an oxide layer which would inhibit growth. Another advantage of using Pd tips is that its crystal lattices observed in 3D atom probe image can be used for dimension calibration in image reconstruction. An $I$-$V$ curve from cyclic voltammogram for polyphenol growth is illustrated in Fig. 4.2 (a). Electropolymerization was started with the first anodic scan, which generated the largest peak at 0.7 V, corresponding to the oxidation potential for the phenol monomers. The polymerization reaction was demonstrated in (4-2).

\[
\begin{align*}
\text{Oxidation of a phenylate anion converts it into a cation radical, which starts the}
\end{align*}
\]

\[
\begin{align*}
\text{polymerization}^{34} \text{ with other monomers to form predominantly } para-\text{-linked polymer. In the}
\end{align*}
\]

\[
\begin{align*}
\text{subsequent potential cycles, current passing though the tip surface decreased drastically,}
\end{align*}
\]

\[
\begin{align*}
\text{indicating the formation of insulating polyphenol film. After 10 cycles of deposition, the film}
\end{align*}
\]

\[
\begin{align*}
\text{growth became very slow, showing the reaction’s self-limiting characteristic. The film was}
\end{align*}
\]

\[
\begin{align*}
\text{very thin so it could not be directly observed in an optical image Fig. 4.2 (b).}
\end{align*}
\]
Figure 4.2 I-V curve of phenol electopolymerization by cyclic voltammogram in 40 mM phenol solution was demonstrated in (a). The black arrow indicated the change in current with each cycle during the film growth. An optical image on a Pd tip after coating was shown in (b). The film was too thin to be observed.

To further confirm the formation of polyphenol coating on the end of the Pd tip, TEM imaging was performed as shown in Fig. 4.3. The heavy metal atoms comprised the dark region, which represented the shape of the Pd tip. The lattice fringes were not visible because of the interference from coated layer. Polyphenol coating also covered the side surface of the
tip. Thus Pd tip was behind a layer of coating on the tip shank. The layer thickness in this sample was estimated to be about 8 ~ 10 nm. The variation of the thickness is less than 15% measured from the image. It was also confirmed that the polyphenol films were able to cover the tip apex.

![TEM image of a polyphenol coated Pd tip](image)

**Figure 4.3. TEM image of a polyphenol coated Pd tip. Dark area was the body of Pd tip. A grey layer on the top of metal surface was the polymer coating of 10 nm thick.**

A polyphenol coated palladium tip was examined by the atom probe microscope using laser pulse evaporation. The voltage and mass spectrum histories were given in **Fig 4.4**. The voltage history shows that the standing voltage $V_{dc}$ drastically increased after approximately 400,000 ions detected. Compared with the mass history one can see that this region corresponds to the shift region where low mass ions decreased and Pd isotopic peaks
Figure 4.4. Voltage (a) and mass spectrum history (b) recorded from an atom probe analysis on a polyphenol coated Pd tip. In the voltage history (a), a transitional region was found indicating evaporation shift from coated layer to the metal substrate. This interface was confirmed by the mass spectrum history (b). Different ions appeared in the two sides of the interfacial region. Starting voltage from metal phase was used to estimate the tip radius of curvature in the sequential volumetric reconstruction.

at 102 ~ 110 (m/n) increased significantly. The region reflects that the surface evaporation was shifting from the polymer layer to the metal substrate. At early stages of the experiment, only the polymer layer was exposed to evaporation. It was confirmed by absence of Pd signal
in the first 400,000 ions in mass history (Fig 4.4b). Most of ions were located in low (m/n) region below 100, indicating some of the polymeric material was fragmented into small ions. Apparently the polymer layer was evaporated under lower and stable $V_{dc}$. In the mass history (fig. 4.4b), besides the clear lines which corresponding to specific ions, there are some hits observed randomly distribution in the chart. These ions could not be detected appropriately by the mass spectrometer probably due to the complex fragmentation of the polymeric material. But in the cumulative mass spectrum (fig. 4.5) one can see that they present as the noise floor which are not severe and interrupting the peak identification. After crossing the polymer/metal interface, there is still some amount of low-mass ions detected. They are likely from evaporation of the polymer layer coated on the shank of the Pd tip.

The mass spectrum of both PPO and PAPO are given in figure 4.5 for comparison. The mass spectrum of PPO in Fig. 4.5a is the cumulative spectrum of the mass history in Fig. 4.4b. The mass spectrum from the PAPO film is given in Fig. 4.5b. The polymer fragments including CH$_x$+, O+, H$_2$O+, C$_2$H$_x$+, CH$_x$O+, C$_3$H$_x$+, C$_3$H$_5$+, C$_6$H$_6$+, C$_2$H$_x$O+ , C$_6$H$_6$O+ and Pd atoms are detected in PPO layers. The polymer fragments of NH$_x$, C$_n$H$_x$+, C$_n$H$_x$O+, C$_n$H$_x$N+ and monomer C$_n$H$_x$ON+ are found in PAPO layers.

In Fig. 4.5a, major peaks were observed at m/z of 12, 15, 18, 19, 24, 28, 43 and 78. The fragments appearing in the low mass region are primarily due to fragmentation of PPO. The group of peaks in 102 ~ 110 (m/n) correspond to the Pd isotones
from the metal substrate. Fragments such as $\text{CH}_x^+$, $\text{C}_2\text{H}_x^+$, $\text{C}_3\text{H}_x^+$, $\text{C}_5\text{H}_x^+$, $\text{C}_6\text{H}_x^+$, $\text{C}_6\text{H}_6^+$, $\text{O}^+$, $\text{CH}_x\text{O}^+$ and $\text{C}_2\text{H}_x\text{O}^+$ are generated by chain cleaving at different positions. The heaviest peak

Figure 4.5. The mass spectrums from the atom probe analysis of a PPO coated palladium tip (a) and a PAPO coated Pd tip (b). The polymer fragments including $\text{CH}_x^+$, $\text{O}^+$, $\text{H}_x\text{O}^+$, $\text{C}_2\text{H}_x^+$, $\text{CH}_x\text{O}^+$, $\text{C}_3\text{H}_x^+$, $\text{C}_5\text{H}_x^+$, $\text{C}_6\text{H}_x^+$, $\text{C}_6\text{H}_6^+$ and Pd atoms are detected in PPO layers. The polymer fragments of $\text{NH}_x$, $\text{C}_n\text{H}_x^+$, $\text{C}_n\text{H}_x\text{O}^+$, $\text{C}_n\text{H}_x\text{N}^+$ and monomer $\text{C}_n\text{H}_x\text{ON}^+$ are found in PAPO layers.
at 78 indicated the presence of monomer ions C₆H₆ from polymer chains. A small peak at 94 corresponds to intact monomer ion C₆H₆O⁺. The peaks at 12 and 24 (m/n) are observed suggesting that polymer chains were also decomposed into C and C₂ ions. Peaks of 17~19 represented the hydroxyl based groups from residual water molecules. Another major peak at 15 was considered as mainly from ¹⁵CH₃ because of its high stability. Peaks centered at 28 and 43 were identified as C and C₂ fragments containing O from phenol unit fragmentations. In later stage of the experiment, Pd peaks became predominant while the low mass peaks were diminishing, revealing the transition from polymeric material to palladium substrate.

Based on the structure of PAPO, the bond cleavages occurring on different positions in the surface evaporation can generate fragments including NHₓ, CₙHₓ⁺, CₙHₓO⁺, CₙHₓN⁺ and monomer CₙHₓO⁺. This is different from PPO films for which the fragments can only be CHₓ, CₙHₓ⁺ and CₙHₓO⁺. The peaks identified from the PAPO film and PPO film are list in Table 4.1 for comparison. From the comparison one can see that both mass spectrums show the low mass regions are comprised of groups of peaks 1 (u/e) from each other in the ranges of 17 ~ 19, 24 ~ 29, 36 ~ 45, 48 ~ 55, 78 ~ 81 and 107 ~ 109 (for PAPO). They correspond to the polymer fragments with losing different numbers of H atoms. But the peaks need to be interpreted differently for each polymer depending on their compositions.
Table 4.1. Comparison of the mass spectrums from PPO and PAPO. Peak identification for PPO fragments in Fig. 4.5a. As comparison, the major peaks from a mass spectrum of PAPO film in Fig. 4.5b are also given.

<table>
<thead>
<tr>
<th>u/e</th>
<th>PPO Fragments</th>
<th>PAPO Fragments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1~3</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>12</td>
<td>C+</td>
<td>C+</td>
</tr>
<tr>
<td>14~15</td>
<td>CHx</td>
<td>NHx</td>
</tr>
<tr>
<td>17~18</td>
<td>H3O</td>
<td>H3O</td>
</tr>
<tr>
<td>26~29</td>
<td>C2Hx or CHxO</td>
<td>C2Hx+CHxO+CHxN</td>
</tr>
<tr>
<td>36~45</td>
<td>C3Hx or C2HxO</td>
<td>C2HxO + C2HxN + C3Hx</td>
</tr>
<tr>
<td>48~52</td>
<td>___</td>
<td>C4Hx</td>
</tr>
<tr>
<td>62~65</td>
<td>C5Hx</td>
<td>C4HxN</td>
</tr>
<tr>
<td>78~80</td>
<td>C6Hx</td>
<td>C6HxN + C6HxO</td>
</tr>
<tr>
<td>107~109</td>
<td>___</td>
<td>C6HxON</td>
</tr>
</tbody>
</table>

After proper peak identification, three dimensional image of the PPO coating was reconstructed as in Fig. 4.6a. The top layer was composed of the low mass ions, sitting on top of the pure Pd substrate. Depth concentration profiles of elements are given in Fig. 4.6b. Isoconcentration surfaces of 50% Pd and 50% polymer fragments are constructed in Fig. 4.6c and d. The isoconcentration surfaces showed clearly two phases. The lattice spacing of Pd substrate was also checked to verify the reconstruction. In Fig. 4.6e one can see that clear lattice planes were not easy to be visualized. There were small amount of Pd ions found on the top of Pd substrate as seen in Fig. 4.6c. From a specific angle of view in the 3D image,
Figure 4.6. Three-dimensional reconstruction of analyzed volume from a polyphenol coated Pd tip was presented as a dot graph (a). Blue dots referred to the detected Pd atoms, green dots for the polymer fragments. The elemental concentration profiles along the depth were plotted in (b). 50% isoconcentration surfaces of polymer coating and Pd substrate were constructed in (c) and (d) respectively. The two regions were clearly separated. Pd lattice spacing was found in the reconstructed image from a proper angle of view (e). Measured spacing in the picture was used to verify the image reconstruction.
lattice layer with lots of vacancies and out-of-plane atoms could be seen. The measured
lattice spacing was close to the value from TEM images. In the image reconstruction, the tip
radius of curvature at each depth was calculated in the software based on the single phase
model in which the evaporation field $F$ in equation $r = \frac{V_{DC}}{k*F}$ adopted was the value
measured for pure palladium tips. The evaporation fields of polymer fragments are different
from $F_{Pd}$, but by now there is no available value for variety of polymeric materials. From the
voltage history (fig. 4.4a) we can see that the $V_{DC}$ in polymer region is around 2000V but
increased to over 6000 V in metal substrate region. Assuming the radius of curvature was not
changed drastically from the TEM image, the $F_{polymer}$ can be estimated as only 1/3 of $F_{Pd}$.

Therefore the reconstructed image by single phase model inflated the thickness of the
polymer layer. The corrected thickness should be 1/3 of the value in the 3D image (fig. 4.6a),
about 10 ~ 15 nm, which is very close to the value from the TEM image.

The elemental concentration profiles showed a clear transition region from the depth.
Above the interface, C, H and O were predominant with less than 1% Pd. C, H and O should
come from the polymer layer. It was found that the C:O ratio did not agree with the elemental
contents in the polyphenol chains. The lowest O% read above the interface was 6.2%, while
the highest C% was 30%, therefore the C:O ratio was a little less than 5, which was lower
than 6. O atoms can also come from residual water molecules. Inflated O percentage along
the depth down to 40 nm suggested that O atoms from water molecules existed in polymer
phase. So the spikes of O% around 7 nm and 40 ~ 48 nm interfacial region could be explained as higher H$_2$O contents in these regions.

The results show that electrodeposited polyphenol layer on metal tips can be visualized by atom probe tomography. In the analysis, the polymer layer was broken into fragments in surface evaporation. The fragments can be identified to their chemical compositions in the mass spectrum analysis. Several approaches were used to verify the peaks interpretation by combining the spatial distribution of the ions and comparing C:O ratio to the stoichiometry of the polymer. In the 3D reconstructed images, the polymer layer can be clearly distinguished from the metal substrate. This result shows the potential of the atom probe technique for more complicated organic systems.

### 4.3.2 Polyaniline analysis

Since there is no similar report was found about polyaniline (PANi) film formation of highly curved surfaces as atom probe tip surfaces, we did some preliminary investigations on depositions. Two problems were found regarding the morphologies of forming films: the first one is that the initial films were too thick and rough as shown in Fig. 4.7 (b). This kind of rough coating created multiple evaporation spots, which would severely deteriorate the mass spectrum resolution and also effect the image reconstruction based on the single emitter assumption. The second problem is that coated layer on sharp tips prepared with standard
deposition procedures were preferentially formed on the side of tips instead of covering the tip apex where the tip radius of curvature was less than 50 nm, as in Fig. 4.1 (a and b). As mentioned before, the conducting polymers tend to overgrow on the sharp tips form thick and irregular shape. Because of the small radius of curvature the tip apex is hard to cover by thick films. To avoid preferential growth, we minimized the contact area of the specimen with monomer solution during polymerization by lifting the tip to form a meniscus of liquid at the tip end. Polymerization was therefore confined in the tip terminal. To prepare thinner films, we used diluted concentrations of aniline to suppress the rate of polymerization in surface region and found 40 mM aniline in 0.5 M H₂SO₄ was appropriate concentration to form thin and uniform coatings (fig. 4.7f). PANi thin film on the Pd tip end showed green color. When the film grew thicker, its surface
Figure 4.7. I-V curve of aniline electropolymerization by cyclic voltammogram in 0.5 M H2SO4 was demonstrated in (a). The black arrow indicated the growth direction. An optical images (b) showed a rough and thick coatings of polyaniline (PANI) on a sharp Pd tip. Formation of preferential coating on the side of sharp tip was illustrated in (c and c). A improved method for coating the end of Pd tips was demonstrated in (e). An optical image of the resulting coatings on a Pd tips was presented (f). Green color came from PANi coating under illumination. The tip end was found being covered by the polymer.
became rough and therefore the color looked darker. The optical images showed successful deposition of PANi on the sharp Pd tips.

The atom probe analysis was performed on a PANi coated Pd tip. A voltage history and a mass spectrum history from an atom probe analysis are shown in Fig.4.8. The transition region in the voltage history jumping from 3000 V to 5000V suggests a phase change of the field evaporation from polymer to metal substrate in the ion sequence range of 600,000 ~ 700,000 as shown in Fig. 4.8a. This is consistent with the observation from the mass history in Fig. 4.8b. In the same region the low mass peaks disappear while the Pd isotopic peaks become predominant. In the low mass region, comparing to the mass history for the PPO coated samples, much greater amount of the random hits appears. This indicates the greater roughness of the PANi films which causes wider velocity distribution of the evaporated ions from the surface. In the voltage history, it can be found that the voltage for polymer layer evaporation is lower than that for metal surface. Since the sample radius does not change significantly, the evaporation voltages correspond to the evaporation fields for the two phases, the polymer layer and the Pd substrate. The evaporation field $F_{Pd}$ for pure palladium can be found from literatures$^{43}$. But for variety of polymers their evaporation fields are absent. As mentioned in the previous section, the reconstruction software does not have the data for polymers either. But the thickness of the polymer layer can be estimated by adjusting $F_{polymer}$ according to $F_{Pd}$. 
Figure 4.8. Voltage (a) and mass spectrum history (b) recorded from an atom probe analysis on a PANi coated Pd tip. In the voltage history (a), a transitional region was found indicating evaporation shift from coated layer to the metal substrate. This interface was confirmed by the mass spectrum history (b). The cumulative mass
spectrum is given in (c).

Close estimation of PPO film thickness was obtained in the previous analysis. Here the $V_{\text{polymer}}$ in fig. 4.8a is about 2500 V while $V_{\text{Pd}}$ about 5000 V. So the $F_{\text{polymer}}$ is estimated as $1/2$ of $F_{\text{Pd}}$.

In the mass spectrum, fragments from the polyaniline chains

\[
\begin{array}{c}
\text{are found including } H^+, C^+, NH_x^+, H_xO^+, CH_xN^+, C_2H_x^+, C_3H_x^+, \\
C_4H_x^+, C_5H_x^+ \text{ and } C_2H_xN^+. \text{ The possible chain cleavages are illustrated in Figure 4.9.}
\end{array}
\]

\[\text{Figure 4.9. Illustration of formation of fragments from polyaniline chains in surface evaporation.}\]

The list of peaks identifications is given in Table 4.2. The intensity of the peaks are normalized based on the total count in the range of 0 ~ 80 (m/n) which includes all the major peaks of polymer fragments.
Table. 4.2. Peak identifications in the mass spectrum of polyaniline coating. The intensity of the peaks are normalized based on the total count in the range of 0 ~ 80 (m/n) which includes all the major peaks of polymer fragments.

<table>
<thead>
<tr>
<th>m/n</th>
<th>Ion type</th>
<th>Peak intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>0.0717</td>
</tr>
<tr>
<td>12</td>
<td>C</td>
<td>0.0067</td>
</tr>
<tr>
<td>14 ~ 16</td>
<td>NH_x</td>
<td>0.0163</td>
</tr>
<tr>
<td>17 ~ 19</td>
<td>H, O</td>
<td>0.2235</td>
</tr>
<tr>
<td>26</td>
<td>CN</td>
<td>0.0307</td>
</tr>
<tr>
<td>27 ~ 29</td>
<td>CH_xN</td>
<td>0.1662</td>
</tr>
<tr>
<td>30</td>
<td>C_2H_6</td>
<td>0.0679</td>
</tr>
<tr>
<td>36 ~ 43</td>
<td>C_3H_x</td>
<td>0.2636</td>
</tr>
<tr>
<td>48 ~ 55</td>
<td>C_4H_x</td>
<td>0.0744</td>
</tr>
<tr>
<td>60 ~ 65</td>
<td>C_5H_x</td>
<td>0.0789</td>
</tr>
</tbody>
</table>

Voltage history was chosen to simulate the sample radius, which was based on the relationship stated in equation 2-4: \( r = \frac{V_{DC}}{k \cdot F} \). The dimension calibration was conducted by comparing lattice spacing of Pd substrate in reconstructed volume in Fig. 4.10c with the values from TEM images in Fig. 2.13 and theoretical calculation from equation (3-3) as demonstrated in Chapter 2. A trial and error procedure was conducted to adjust the tip radius and shank angle to achieve appropriate volumetric reconstruction. A direct measure of Pd crystal spacing was found 0.25 nm in the reconstruction image. This value is close to the one from computer reconstruction and equaled to the values from TEM images. After the reconstruction image was established, other analysis were able to be applied to identify the polymer metal substrate interface. 90% Pd iso-concentration surface, 90% PANi
iso-concentration surface and Pd lattice spacing are constructed as in Fig. 4.10c and d.

Analyzed PANi film was about 40 nm thick. Because the reconstruction software does not take account the difference between $F_{\text{polymer}}$ and $F_{\text{Pd}}$, and the dimension is estimated based on $F_{\text{Pd}}$, the thickness of the PANi film should be close to 20 nm.

In the 1D concentration distributions, the fragments are broken into individual atoms. The elemental concentrations are calculated along the depth. The PANi/metal interface can be clearly identified in the figure. At 40 nm deep, the concentrations of O, N, C, and H decrease drastically while the Pd concentration increases over 95%. It shows that the polymer layer was deposited on the metal surface and evaporated first in the atom probe analysis. The concentrations of elements from the polymer are almost constant in the upper layer. Their ratios are close to $C_6H_{8,6}N$, which is consistent with the PANi’s structure ($C_6H_6N$). The extra H should come from the water residuals in the polymer matrix.
Figure 4.10. Three-dimensional reconstruction of analyzed volume from a polyaniline coated Pd tip was presented as a dot graph (a). Blue dots referred to the detected Pd atoms, green dots for the polymer fragments. The elemental concentration profiles along the depth were plotted in (b). 90 % isoconcentration surfaces of polymer coating and Pd substrate were constructed in (c) and (d) respectively. The two regions were clearly separated. Pd lattice spacing was found in the reconstructed image from a proper angle of view (e). Measured spacing in the picture was used to verify the image reconstruction.
Figure 4.11 shows a C:N ratio profile along the depth. The ratio is constant at 6 along depth. This demonstrates that the polymer fragments can be identified accurately.

![Figure 4.11. Elemental carbon to nitrogen ratios along depth. The horizontal line indicated the theoretical ratio of C to N in polyaniline chains. Interfacial region was circled. The measure C:N ratios along depth agreed with the theoretical value.](image)

In the interfacial region, the ratio jumped irregularly, suggesting different evaporation behaviors across the phase boundary.

In this section, the results show that electrodeposited PANi layers on metal tips can be visualized by atom probe tomography. In the analysis, the polymer layer was broken into fragments in surface evaporation. In the 3D reconstructed images, the PANi layer can be clearly distinguished from the metal substrate. This result shows the potential of the atom probe technique for more complicated organic systems. The results also show that the surface evaporation of the polymer fragments is important steps which will affect the peak
identifications. In the next section, the laser energy and temperature effects on polymer fragmentation will be investigated.

**4.3.3 Laser pulse energy and temperature effects on mass spectrum**

Since no report has been found about atom probe analysis on PANi, information on its mass spectrum can only be found in normal mass spectrometer analysis\textsuperscript{44-46}. These analysis are focus on intact monomer, dimer or larger molecular ions, instead of small fragments from high degree fragmentation of the polymers. In Maruyama\textsuperscript{7} and Nishikawa\textsuperscript{47} reports on polypyrrole and polystyrene, mass-to-charge ratio peaks showed predominantly in the low mass region smaller than a monomer, indicating deeper fragmentation occurred under high potential fields. We expected similar level of fragmentation would be seen under laser pulsing in the LEAP microscope. On the other side, Maruyama and Nishikawa’s experiments on polypyrrole and polystyrene by atom probe field ion microscopes showed inconsistent results\textsuperscript{47}. Maruyama et al. found monomer, dimer and trimer fragments from the mass spectrum of a polypyrrole sample, while in Nishikawa’s work showed only low mass fragments were observed in the mass spectrum which they thought were oxygen containing species not from the polymers. After we successfully obtained polyaniline coated on Pd tips, the influence of laser pulse energy and temperature on surface evaporation and polymer fragmentation can be investigated.
The mass spectrums obtained under 53.6 K from three laser pulse energies on one sample are presented in Fig. 4.12a–b. The ion counts were normalized based on the total detected ions so the peaks corresponded to the intensities of ions and can be compared among the spectrums. The testing temperature was fixed at 53.6 ~ 53.7 K. Three mass spectrums were obtained from three consecutive tests under very similar $V_{dc}$, so the laser energy fractions normally used to describe laser energy contribution to the ion evaporation were based on the same standing voltage. It was found that even under low level of laser pulse energy (0.2 nJ), primarily only fragments smaller than a single monomer were observed. The $M_w$ of aniline monomer is 92. It suggests that the polymer fragmentation was severe. Since the polymer sample was pre cleaned after deposition and degassed in $10^{-6}$ Pa under room temperature for overnight, the amount of surface contaminants such as CO, H$_2$O and acids should be eliminated. During the atom probe analysis, polymer sample was evaporated under $10^{-8}$ Pa. Therefore the majority of ions detected by the mass spectrums were believed to be from the polymer instead of from ion recombination.

From preliminary inspections of the mass spectrums in Fig 4.12, it was observed that with increasing laser energy, the heavy peaks diminished while light peaks at 12 amu and 15 amu increased. Groups of peaks separated by 1 amu were observed in the ranges of 26~ 30, 40 ~ 45 and 50~56, which are usually similar fragments with different numbers of H atoms. These fragments are composed of carbon and nitrogen atoms, with carbon and nitrogen from polyaniline. Large peaks at 17 ~ 19 indicated the existence of H$_2$O molecules. First the
Figure 4.12. The mass spectrums obtained from three consecutive atom probe tests under 53.7 K on a PANi coated Pd tip. The tests were performed under three levels of laser pulse energy, 0.2 nJ (a), 1.0 nJ (b) and 5.0 (c). V_{DC}’s were similar in the tests. The change of peak patterns indicated the degree of fragmentation of PANi under increasing laser heating.
largest peaks appeared in the mass spectrums were those at 44 and 45, 27~29, 17~19, 15, 12 and 6. Peaks at 6 and 12 are carbon ions with charge states +1 and +2 respectively. Peaks 17~19 are \( \text{OH}^+ \), \( \text{H}_2\text{O}^+ \) and \( \text{H}_3\text{O}^+ \). Peaks at 27~29 and 44~45 had variable relative intensities depending on laser energy levels, which are larger polymer fragments.

The peaks shift to light mass region with increasing laser pulse energy. With peak identifications, the relative intensity changes of fragments can be plotted against three levels of laser energy as shown in Fig. 4.13. The most obvious trends observed from the charts are that the pure carbon ions \( \text{C}^{2+} \), \( \text{C}^+ \) and \( \text{C}_2^+ \) drastically increased under the highest level of laser energy 5 nJ. The intensities of other heavy peaks around 40 ~ 45, 51~54, 64~65 and 77~78 kept decreasing with increasing laser energies, suggesting the level of fragmentation increased with increasing energy input and smaller fragments becoming predominant.
Figure 4.13. Relationship between peak intensities and laser pulse energy from extracted from Figure 3.3 under 53.7 K. Light carbon ions in (a) showed increasing intensities, while intensities of two heavy ions decreased with increasing laser pulse energy. Ions in the range of 15~30 amu (b) showed decreasing trends except for the peak at 27 amu, indicating it was another major fragment under very high laser power. Peaks in the range of 41 ~ 78 (c and d) all showed basically decreasing intensities with increasing laser power, suggesting fragmentation became severer under high laser power.

Another set of similar experiments were carried out under a temperature of 32.3 K. Similar peaks are found in the mass spectrums as for 53.7 K. The mass spectrums can be
Figure 4.14. The mass spectrums obtained from three consecutive atom probe tests under 32.3 K on a PANi coated Pd tip. The tests were performed under three levels of laser pulse energy, 0.2 nJ (a), 1.0 nJ (b) and 5.0 (c). V_{DC}'s were similar in the tests. Similar change in peak pattern as in Figure 3.3 was found.
found in Fig. 4.14. The investigation on laser energy influence was illustrated in Fig. 4.15.

The peak shifting along increasing laser energies also showed similar trends. Temperature does not affect the polymer fragmentation significantly.

Figure 4.15 Relationship between peak intensities and laser pulse energy from extracted from Figure 3.5 under 32.3 K. Light carbon ions in (a) showed increasing intensities, while intensities of two heavy ions decreased with increasing laser pulse energy. Ions in the range of 15–30 amu (b) showed decreasing trends except for the peaks at 27 and 28 amu, indicating they were major fragments under very high laser power. Peaks in the range of 41–78 (c and d) all showed basically decreasing intensities with increasing laser power, similar as that under higher temperature.
These results indicate that the laser pulse energy significantly affects the fragmentation of the polymer in the atom probe analysis. Under higher laser energy, the polymer chains were decomposed into smaller ions, while with lower laser energy larger fragment can be formed. Changing the laser energy also provides an approach to discriminate polymer evaporation from other small molecule adsorbates such as H$_2$O or CO$_2$. Testing under lower laser energy is favorable to the sequential mass spectrum interpretations since larger fragments easier to be identified while smaller fragments are not easy to be distinguished from adsorbed residual molecules. The temperatures tested in this work do not affect the polymer evaporation significantly.

4.4 Conclusions

Two types of electrodeposited polymers, polyphenol as an insulting polymer and polyaniline as an example of conducting polymers were successfully resolved by atom probe analysis for the first time. In sample preparation, the polymers were electrochemically deposited onto sharp atom probe tips in forms of thin film. Metal tips made of Pd were used as conductive surfaces in electropolymerization. Cyclic voltammetry curves showed the growth of films. The CV charts showed similar growth of polymers as depositions performed on flat surfaces, but special efforts have been endeavored to coat thin and smooth polyaniline layers on tip apex with extremely high radius of curvature because the conducting polymer tended to overgrow to form thick and rough films. Preferential growth of PANi on tip side
was avoided by minimize contact area of tips with solution in electropolymerization.

Formation of polyphenol coating did not present similar difficulties because of its self
limiting growth mechanism, which favored formation of smooth but thin films. The
formation of films on sharp tips was first confirmed by optical microscope and TEM images.
Then they were analyzed sequentially by the atom probe microscope with laser pulse
evaporation. The polymer coatings and Pd substrates were observed clearly in the 3D images
and 1D elemental concentration profiles along the depth.

In the current image reconstruction approach, the dimensions of the analyzed volume,
especially the radius is determined by the equation: \( r = \frac{V_{DC}}{k \cdot F} \). Current reconstruction
methods are based on the single component samples in which the evaporation field can be
obtained from the pure materials. But for polymer coatings on the metal surfaces, the
evaporation fields for the two phases are significantly different, as observed in the voltage
histories of PPO and PANi samples. The dimensions of the 3D images are calculated based
on the metal evaporation field, which was higher than the polymer films. Therefore,
according to the equation, the thicknesses of polymer films were inflated. Although currently
there is no evaporation field data for variety of polymer, we found that it can be estimated
from the evaporation voltage. Since the diameters of the samples do not change drastically as
observed from the TEM images, the evaporation field of polymer layers are can be found by:

\[
F_{\text{Polymer}} = \frac{F_{\text{metal surface}} V_{\text{Polymer}}}{V_{\text{metal surface}}}
\]
In the 3D images reconstructed based on single phase model, the thickness of polymer layers need to be adjusted according to the ratio: \( \frac{F_{\text{Polymer}}}{F_{\text{metal surface}}} \). In PPO images, adjusted film thickness by this method agreed with the one from the TEM image.

Laser energy and temperature effects on mass spectrums were investigated. With increasing level of laser pulse energy, heavy peaks diminished while light peaks corresponding to pure carbon ions increasing drastically, suggesting high laser pulse energy in the instrument setting could cause severe fragmentation of polymers. The temperatures tested in this work did not affect the polymer evaporation significantly.

4.5 References


(40) Chen, X. H.; Hu, Y. B.; Wilson, G. S. Glucose microbiosensor based on alumina sol-gel


CHAPTER 5. ATOMPROBE ANALYSIS OF NANOPARTICLE-ENCAPSULATED FILMS

5.1 Introduction

Nanoparticles have been extensively studied because of their unusual size, shape and composition related properties. Gold nanoparticles (Au NP) are one of the most widely used metal nanoparticles\textsuperscript{1}. They have been widely used as catalysis\textsuperscript{2-8}, biological applications\textsuperscript{9-16} and nonlinear optics\textsuperscript{17-21}. Unlike bulk gold, gold nanoparticles show unique properties. Au NPs of 1–5 nm supported on oxides such as iron-oxide\textsuperscript{22,23}, silica\textsuperscript{24} or titania\textsuperscript{25} were found reactive in CO oxidation and hydrogenation. In bio-related applications, they are used for purposes of sensing\textsuperscript{26}, labeling\textsuperscript{27,28}, delivery\textsuperscript{29} and heating\textsuperscript{30}. A highly selective diagnostic method for DNA was developed using Au particles of 13 ~ 17 nm utilizing the optical properties from their distance-related Surface Plasmon bands\textsuperscript{31}. A conducting polymer with well dispersed gold nanoparticles as dopants has a large third-order nonlinear optical susceptibility proportional to the particle radius, making it a good candidate for use in nonlinear optical devices\textsuperscript{19}. With increasing number of new developments and configurations of gold nanoparticle systems, novel characterization method is of great interest.

In the previous chapter we demonstrated that several polymer thin films coated on palladium tips by electropolymerization were successfully visualized in atom probe analysis.
With the aid of laser pulsing, the insulating layers were able to be evaporated into polymer fragments. Spatial positions of the fragments in the polymer matrices were determined by the position sensitive detector. Their chemical identities were sequentially determined in mass spectrum analysis. Three dimensional images of the polymer layers could be achieved based on the information. Proper reconstructions of the polymers were also confirmed by their relative position to the palladium substrates and distributions of carbon and oxygen elements.

Poly(aminophenol) (PAPO), a derivative of polyphenol is a similar type of electrodeposited polymer having been widely studied for enzyme and protein immobilization\textsuperscript{32-44}, sensor developments\textsuperscript{45} and surface protection\textsuperscript{46-49}. Due to its self limiting growth under external potential in electrodeposition, thickness of the resulting film on a conducting surface is normally less than 100 nm. A nice property of the film is its ability to cover highly irregular surfaces\textsuperscript{50}, which is vital for developing thin layer coating on already tiny surface of the atom probe tips.

Based on the properties, we developed a novel configuration of sample design which enables analysis of nanoparticles by the atom probe microscope for the first time. There are several advantages of the design. Coated tips with well defined geometrical shape are important for atom probe analysis. It ensures predictable evaporation sequence of the surface ions and therefore precise three dimensional images can be reconstructed. Metal tips can be easily prepared into the shape with sharp end and a round head via standard tip preparation methods, which can serve substrates for coatings. Thin polymer layers with uniform
thickness deposited on top of a metal tip surfaces are able to preserve the shape of metal tips, which also eliminates reshaping of the samples. Further more, the nanoparticles can be incorporated in the polymer layers during electrodeposition of the films. This provides a very easy approach to deliver the nanoscale analytes onto the region of interest on the tips.

Figure 5.1. Schematic of proposed sample design for atom probe analysis. The sample configuration was illustrated in (a). The electrodeposition process is demonstrated in (b).

In this work, we choose gold and platinum nanoparticles as examples to demonstrate the ability of the atom probe microscopy. Briefly, electrodeposited thin layers from 3-aminophenol and aniline will be uniformly coated on metal tips as shown in Fig. 5.1. In the poly(3-aminophenol) film, the target nanoparticles can be dispersed in precursor solution before deposition, and encapsulated into the polymer layer during electrodeposition of
monomers. In the polyaniline film, the metal particles will be impregnated into the polymer layer by in-situ reduction from the metal salt. Formation of the polymer coatings also works as a process for extracting nanoparticles from their solution. Coated samples are ready for sequential atom probe analysis. When a sample surface is evaporated during analysis, the polymer layer is acting as a supporting material to immobilize nanoparticles. The sample design in this report is not limited to analyze metal nanoparticles, but suitable for any type of nanoscale objects including other metallic or inorganic nanoparticles with multiple composition and complex structures such as core-shell configuration, and macromolecules or possible biomolecules.

5.2 Experimental Section

5.2.1 Material and Reagents.

Glacial acetic acid (a.c.s., Fisher), perchloric acid HClO$_4$ (70%, Fisher), 3-aminophenol (98%, Aldrich) and monobasic sodium phosphate (a.c.s., Fisher) were used as received. Non-functionalized Nanogold® Particles (1.4 nm diameter) was ordered from Nanoprobes (Yaphank, NY). Palladium wire (0.20 mm, 99.9%) was purchased from Structure Probe, Inc. (West Chester, PA). Fresh electro-polishing fluid was prepared every time before wire etching by mixing perchloric acid with glacial acetic acid (1:4). Solutions used for electrochemical polymerization of 3-aminophenol were made by dissolving 40 mM corresponding precursors into 0.1 M monobasic sodium phosphate. pH of the solution were
adjusted to neutral by 1M NaOH. The solution used for encapsulating gold nanoparticles was prepared by adding about 0.5 nmol Nanogold solid into the 3-aminophenol solutions. All aqueous solutions were prepared in 18 MΩ cm deionized water (NANOPure, Barnstead, Dubuque, IA).

5.2.2 Metal tip Preparation.

Detailed tip preparation has been explained in chapter 2. A brief description on the procedure is given here. Typically two atom probe specimens were made from a piece of 10 mm long palladium wire (0.2 mm diameter) in each electro-polishing process. The wire was etched gradually with a Pt ring electrode in universal polishing fluid with DC voltage of 4 V. A neck region formed and became thinner until being fractured by its own weight. The specimens were subsequently rinsed through deionized water, methanol and acetone to remove the residuals, and then stored in the container. To achieve atomic smooth surface, Pd tips were pre-run in the atom probe microscope before further treatments. The instantaneous concentration of 99.9% Pd from detection histogram was used as criterion of reaching a clean surface. Smooth surfaces were obtained when there was no hot spot appearing in detector screen. After the pre-run, the specimen was ready to use as substrate for thin film formation.

5.2.3 Preparation of nanoparticle-encapsulated polymer films

The solution used for encapsulating gold nanoparticles in poly(3-aminophenol) was prepared by adding about 0.5 nmol Nanogold solid into 20 ml monomer solution. The
nanoparticles were well dispersed by ultrasonicate for 10 minutes. Electrodepositions of 3-aminophenol with or without gold nanoparticles were performed in a three electrode cell consisting of a Pd tip as working electrode, a commercial Ag/AgCl reference electrode (CH111, CH Instruments, in 3M KCl) and a piece of Pt wire as counter electrode. Electrode potential was controlled via a potentiostat (CHI 900, CH Instruments). Cyclic voltammetric deposition was conducted for film deposition. The potential was scanned in the range of 0 ~ 0.8 V vs. Ag/AgCl for 20 cycles. The scan rate was set at 50 mV/s and a 120 second quiet time was applied before scan started to ensure the tip surface was wetted through.

Polyaniline encapsulated Pt nanoparticles were prepared on metal tips in two steps. First PANI films were electrodeposited by the similar procedure as for PAPO films depositions. Solution of 40 mM aniline in 0.5 M H$_2$SO$_4$ was prepared as deposition precursor. The number of potential cycling and scan rate were adjusted to control the film thickness. The areas of the films on the specimen were checked by the optical microscope. After deposition, the films were rinsed by 0.5 M H$_2$SO$_4$ for 3 times and 5 more cycles were applied in 0.5 M H$_2$SO$_4$ to remove monomers residue. After this, the film was rinsed by deionized water for 3 times and submerged in 50 °C DI water for 3 hours to remove H$_2$SO$_4$. In the second step, the tips coated by PANI films were dipped in 10 mM H$_2$PtCl$_6$ for overnight. After rinsing by methanol for 3 times, the specimens were dipped in methanol to reduce Pt. After the Pt reduction, the specimens were rinsed by DI water for 3 times.
5.2.4 TEM imaging

Preliminary checks on shape and integrity of a fresh-polished Pd tips were carried out with an optical microscope. The optical images of the atom probe samples were acquired with a high resolution CCD camera (Sanyo VCC 3972) equipped on a microscope (Nikon). The camera was linked to a personal computer through a frame grabber card (Pinnacle Systems, Inc., Mountain View, CA) and images were captured using commercial software (Studio 8, Pinnacle Systems). The nanoscale features were characterized using a Tecnai G2 F20 scanning transmission electron microscope (STEM) at 200 keV. Chemical composition of films deposited on Pd tips was mapped with an energy dispersive x-ray detector (EDS). Tips were carefully clipped on the sample holder with their sharp end being freely suspended to avoid damage from contacts.

5.2.5 Atom probe microscopy

Specimens with coatings were analyzed by atom probe microscope under laser mode. $V_{DC}$ was applied on the local electrode to create the potential field close to the strength for field evaporation. Instead of utilizing $V_{Pulse}$ to initiate the evaporation, ultrafast laser pulses was superimposed on the specimens to stimulate the thermal evaporation. The laser pulse frequency was 250 kHz. The laser pulse energy was adjusted in the range of 0.2 ~ 5 nJ. The flight length was set as 90 mm in order to detect heavy fragments evaporated under lower voltage. During the test, the $V_{DC}$ was ramped up gradually to maintain the stable evaporation
rate. The emitted atoms or ions passed through the TOF-MS before being detected by the position-sensitive detector. Each emitted fragment’s chemical identity and projected position on the X-Y coordinates of the detector plate was recorded and stored in a computer file. The IVAS software (Imago) was then used to analyze hit records and reconstruct the 3D image of analyzed volume.

5.3 Results and Discussion

The proposed sample design is to use electropolymerization of monomers to extract and encapsulate nanoparticles from solutions, forming a thin and uniform coating on the atom probe tip. The film thickness is expected to be thin and uniform enough to inherit the geometrical shape of the tip. Based on the results of electrodeposited coatings in the previous chapter, the preparation method can be directly used to construct the composite coatings on sharp tips. Varieties of polymers have been investigated by the atom probe microscope including both conducting and insulating polymers. Insulating polymers can easily form thin and uniform coatings because of their self-limiting growth. The conducting polymers tend to overgrow into much thicker irregular films which bring in difficulties in atom probe analysis. We found that PANi can form thin coatings over the tip apex areas with special deposition procedure. In this chapter, we will demonstrate that two types of electrodeposited polymers, conducting and insulating films can be used to prepare the proposed atom probe samples for atom probe imaging of nanoscale analytes.
5.3.1 PAPO encapsulated nanoparticles

In Chapter 4 we showed that phenol could form uniform coating on metal tips by electrodeposition. The phenol derivative, poly(aminophenol) is normally used to immobilize enzymes, proteins and cells. Its amino group is helpful for particle encapsulation. In the work, we chose 3-aminophenol as precursors for nanoparticle encapsulation to demonstrate this method can be used for biomolecules as well. Gold nanoparticles will be encapsulated as analytes since Au atoms are easy to be identified in mass spectrums.

Poly(3-aminophenol) was deposited on palladium tips by similar procedure as for polyphenol depositions. Typical I-V curves for growth of polymers are given in Fig. 5.2a.

![Figure 5.2. I-V curves of cyclic voltammograms for electrodeposition of poly(3-aminophenol) without (a) and with (b) gold nanoparticles. The polymer layers was electrodeposited from 40 mM aminophenol in 0.1 M NaH2PO4 (pH = 7) by cycling potential between 0 and 0.8 V vs Ag/AgCl in saturate KCl for 25 cycles. The scan rate was 0.05V/s.](image-url)
Electropolymerizations were started with the first anodic scan, which generated the largest peak. The peak appeared at 0.55 V vs Ag/AgCl in saturated KCl. The position corresponds to the oxidation potential of aminophenol monomers. The polymerization reaction is illustrated as in equation (5-1). The oxidation of an aminophenylate anion is converted into a radical, which initiates polymerization with other monomers to form predominantly para-linked polymer chains.

\[
\begin{align*}
\text{H}_2\text{N}^+ \text{OH} & \rightleftharpoons \text{H}_2\text{N}^+ \text{O}^- \\
& \xrightarrow{\text{H}^+ + \text{e}^-} \text{Polymerization} \text{H}_2\text{N}^+ \text{O}^- \\
& \text{H}_2\text{N}^+ \text{O}^- 
\end{align*}
\]  

(5 - 1)

In the subsequent scan cycles, current passing through the tip surface decreased drastically, indicating the formation of insulating polymer films. After 10 cycles of deposition, the film growth became very slow, showing its self-limiting characteristic. Fig. 5.2b is the I-V curves from co-deposition of gold nanoparticles with 3-aminophenol. The curve is very similar to the one for pure aminophenol polymerization in Fig. 5.2a. The first anodic peaks for the two cases are at the same position, 0.55V vs Ag/AgCl reference (in 3M KCl). The current densities for the two depositions are very close as well. Because the amount of gold nanoparticles dissolved in the solution was very small, it did not affect the polymerization process significantly.

Detailed investigations on polymer coating with and without presence of gold nanoparticles were carried out by TEM imaging. TEM images from a poly(3-aminophenol) coated Pd tips is shown in figure 5.3a. The dark area in the picture is the tip body. Grey area
on top of the tip surface is the polymer layer. Thickness of the film was estimated to be between 10 and 20 nm. To further confirm chemical identity of the layer, energy dispersive spectrum was obtained. The X-ray was focused in a grey area close to the metal substrate, as shown in the black square in Fig. 5.3a. The EDS spectrum of emitted X-ray from the material in the black box in Fig. 5.3d showed mainly Pd and C signals. The polymer layer appears transparent without embedded granular objects. The images show that electrodeposited PAPO film on sharp atom probe tip was successfully constructed.

Poly (3-aminophenol) film with Au nanoparticles was also examined by TEM as shown in Fig. 5.3b. Presence of gold particles in film was detected with EDS mapping on the film (Fig. 5.3e). In TEM imaging, a Pd tip of about 30 nm diameter (dark area) was found being uniformly covered by a layer of polymer (grey area). Unlike the PAPO film, dark granules about 2 nm can be found embedded in the coating layer, suggesting the presence of metal particles. EDS mapping was focusing on the small areas in polymer layers as shown in the black square in Fig. 5.3b. The spectrum (Fig. 5.3d) from the layer deposited with gold nanoparticles showed predominant Au signal, indicating successful incorporation of Au nanoparticles into poly(3-aminophenol) layer. In the bright field image (Fig. 5.3b), metal particles can be observed above the tip surface. The darkfield image under higher magnification in (Fig. 5.3c) gives clearer views of particles. The sizes of the particles can be measured with image analyzing software ImageJ. The size distribution is given in (Fig. 5.3f). Most of the particles were 1~2 nm which was consistent with the NanoGold description.
Figure 5.3. TEM images of a poly(3-aminophenol) coated Pd tip without (a) and with (b) gold nanoparticles. Dark areas were the Pd substrates in (a and b), while grey areas were the polymer layer about 35–40 nm (a) and 20 nm (b). To confirm the composition of the grey layer, EDS mapping (d and e) were performed in areas of the black square in (a and b). The energy spectrum (d) showed light elements such as C and N, and Pd. No Au shows here. The energy spectrum (e) showed presence of Au. Gold nanoparticles were able to be observed in (c). Their size distribution was given in (f).

A sample with embedded gold particles was examined by atom probe microscope under laser mode with similar procedure for analyzing pure polymer coatings. Two screen snapshots from the position-sensitive detector were taken in an interval of 30 seconds as shown in Fig. 5.4a. The hits with the time-of-flight corresponding to gold atoms in the instant mass spectrum were colored in RED. The hits corresponding to all other ions were
colored in BLUE for clarity. Clusters of red dots in the detector screen were detected. In the test, surface of the composite film was evaporated layer by layer. In the first screenshot, there was only one intact particle. After 30 seconds, the old surface was removed. Three more particles exposed to the evaporation and therefore were detected.

Figure 5.4. Two screenshots of the instant detector window taken in 30 seconds interval. The hits with the time-of-flight corresponding to gold atoms in the instant mass spectrum were colored in RED. The hits corresponding to all other ions were colored in BLUE for clarity.

The evaporation voltage history, mass history and the overall mass spectrum are recorded as in Fig. 5.5a~c respectively. The evaporation and analysis directions are indicated in the graphs by arrows. The PAPO/Pd substrate interface can be identified by comparing the voltage and mass history. Evaporation voltage for polymer layer was lower than Pd substrate. Majority of Au atoms at 197 amu were found in this region, as indicated in Fig. 5.5b. No complex Au containing ions appeared close to the 197 peak. Majority of low mass ions were found in this region as well, indicating their origins from polymer matrix. Comparing the
Figure 5.5. Voltage (a) and mass (b) histories recorded from the atom probe analysis on the PAPO coated Pd tip with encapsulated gold particles by polymer matrix. The mass...
spectrum from a poly(3-aminophenol) layer with embedded NanoGOLD particles on a Pd tip was obtained in (c).

mass history in the same ion evaporation range, one can find significant amount of Pd(H$_2$O)$^+$ at 120~128 amu and Pd(CO)$^+$ ions at 130 ~ 138 amu appearing near the interface, which are the molecular fragments generated from the metal/polymer interface region. The chemical identities can be determined in the mass spectrum in Fig.5.5c since the intensities of isotopic peaks agreed with the natural abundances of Pd isotopes. The intensities of these ions decreased drastically crossing the interface. Passing the interfacial region, the evaporation became more stable on the Pd substrate. The $V_{\text{start}}$ corresponded to the evaporation voltage of the initial Pd surface. It is used to determine the initial tip radius in image reconstruction. In this region, trace amounts of low mass peaks are still observable, which were generated from the polymer layer deposited on the side surface of the tip.

The mass spectrum from the nanoparticle encapsulated PAPO film is obtained from surface evaporation as shown Fig. 5.6. For poly (3-aminophenol) O elements appears in its structures. Therefore the evaporation generated more types of fragments than from polyphenol. In Fig. 5.6, similar small fragments appear in the low mass region of 1 ~ 100 (u/e) as found in other polymer coatings. Since the molecule weight of the monomer is 109.13 g/mol, clear peaks at 107 and 109 correspond to the monomer ions. Those are the largest polymer fragments found in the mass spectrum. A distinct peak found at 197 (u/e) corresponds to Au$^+$ ions, which is clearly separated from the low mass peaks. In higher
mass-to-charge ratio region beyond 197 (u/e), no significant peak was found. The results indicate that the polymer was surface evaporated as fragments no larger than monomers, and no complex ion was formed with Au and polymer fragments. Therefore the low mass peaks correspond to the polymer matrix.

![Mass Spectrum](image)

Figure 5.6 The mass spectrum from the nanoparticle encapsulated PAPO film. The mass spectrum for the composite film is given. The film was electrodeposited on a Pd tip. A full peak identification is listed in Table 5.1.

Based on the structure of the polymer \( \text{H}_2\text{N} \)
\[
\begin{array}{c}
\text{苯} \\
\text{O} \\
\end{array}
\]
\( \text{H}_n \), the bond cleavages occurring on different positions in the surface evaporation can generate fragments including \( \text{NH}_x \), \( \text{C}_n\text{H}_x^+ \), \( \text{C}_n\text{H}_x\text{O}^+ \), \( \text{C}_n\text{H}_x\text{N}^+ \) and monomer \( \text{C}_n\text{H}_x\text{ON}^+ \). The peaks identified from the PAPO film are listed in Table 5.1. One can see that the low mass regions are comprised of groups of peaks 1 (u/e) from each other in the ranges of 17 ~ 19, 24 ~ 29, 36 ~ 45, 48 ~ 55, 78 ~ 81 and 107 ~ 109 (for PAPO). They correspond to the polymer fragments with losing different numbers of H
atoms. But the peaks need to be interpreted differently for each polymer depending on their compositions.

**Table 5.1. Peak identification for poly(3-aminophenol) fragments in Fig. 5.6.**

<table>
<thead>
<tr>
<th>u/e</th>
<th>PAPO Fragments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 – 3</td>
<td>H</td>
</tr>
<tr>
<td>12</td>
<td>C$^+$</td>
</tr>
<tr>
<td>14 – 15</td>
<td>NH$_x$</td>
</tr>
<tr>
<td>17 – 18</td>
<td>H$_x$O</td>
</tr>
<tr>
<td>26 – 29</td>
<td>C$_2$H$_x$ + CH$_x$O + CH$_x$N</td>
</tr>
<tr>
<td>36 – 45</td>
<td>C$_2$H$_x$O + C$_2$H$_x$N + C$_3$H$_x$</td>
</tr>
<tr>
<td>48 – 52</td>
<td>C$_4$H$_x$</td>
</tr>
<tr>
<td>62 – 65</td>
<td>C$_4$H$_x$N</td>
</tr>
<tr>
<td>78 – 80</td>
<td>C$_6$H$_x$N + C$_6$H$_x$O</td>
</tr>
<tr>
<td>107–109</td>
<td>C$_6$H$_x$ON</td>
</tr>
</tbody>
</table>

The peak identifications can be verified by the element distributions in the 3D spaces, as did in the previous chapter. Combination of mass spectrum and spatial information from the position-sensitive detector in the 3D reconstructed images enable us to validate the peak assignments. Because the elements such as C, N, H and O are distributed homogeneously in the single phase polymer matrix, their composition are constant through the polymer layers. In the previous analysis, C to N ratio distribution along depth was used in polyaniline analysis, while C to O ratio for polyphenol analysis. For PAPO mass spectrum analysis, C:O and C:N ratios were constructed along depth since there are an amino group and also an oxygen atom in each polymer unit. The ratio profiles are shown in **Fig. 5.7**. The PAPO/Pd substrate interface was located at 75–80 nm deep from the surface. In the PAPO film, the
C:N ratio was consistent with theoretic value 6 very well. Since the polymer was deposited from the aqueous solution, presence of water molecules in the polymer matrix is inevitable. Therefore the C:O ratio was obtained by excluding O in H$_x$O ions at 17 ~ 19 (u/e). In the range 40 ~ 60 nm, the ratio agreed with the theoretic value 6. The value is larger in other regions such as near the polymer surface and close to the metal/polymer interface. This indicates that the H$_x$O ions at 17 ~ 19 (u/e) are not all from water residuals. When the C:O ratio is close to 6, H$_x$O ions are almost all from the polymer matrix. In the region where the water content is high, the ratio increases towards lack of O atoms. The C:O ratio distribution in Fig. 5.7 suggests that the water content is low in the center of the polymer layers and high near the surface and the metal/polymer interface. Significant amount of C$^+$ ions appeared in the same region suggesting H$^+$ ions generation.

Figure 5.7. C:N and C:O ratio profiles along the depth direction for calculated after peak identification and image reconstruction.
The hit record was processed to construct the 3D dot images in Fig. 5.8.

Isoconcentration surfaces of ions were also calculated and drawn to find boundaries between

Figure 5.8. Reconstructed 3D dot image from a poly (3-aminophenol) coated Pd tip with embedded NanoGOLD particles (a). The scale of the image was set the same with that of the elemental concentration profiles (b). Each dot represented a detected ion colored same as in the isoconcentration surfaces (d ~ g) to distinguish its chemical identity.
Iso-concentration surfaces of Pd (d), polymer fragments (e), HxO ions (f) and Au (g) were also presented separately.

different materials in (d ~ g). Blue surface embraced most of Pd ions (d), representing the surface of metal tip. Polymer fragments with different mass-to-charge ratios (e) were all coded as dark green to construct the coating layer. HxO ions (f) were colored in pink, forming a region mixed with polymer fragments. The pink ions became enriched in the region close to metal surface, suggesting high water content. Gold atoms in red (g) were found primarily in the top most region of the coating, showing successful encapsulation and detection of the particles. Elemental concentration profiles along depth are presented in Fig. 5.8b. There is a clear interface between metal substrate and polymer layer. The O content in the elemental concentration profiles (b) was calculated by excluding O atom in the HxO peaks at 17 ~ 19 amu. While the pink isoconcentration surface in (e) was constructed with only the ions from 17~ 19 amu peaks. But comparing these two distributions it was found their spatial distributions were largely overlap as both had highest concentrations in the depth range between 42 ~ 78 nm. It suggests that the O from the polymer chains were mainly recombined with H to form HxO. Gold particles were found located in the top surface of the films, embedded in the polymer matrix.

A 3D image reconstruction on a thicker composite layer is illustrated in Fig. 5.9. The coating was intentionally prepared thicker in order to trap more nanoparticles. The reconstructed volume (a) is composed of PAPO fragments (green dots) and gold atoms (red
dots). Five cross-sections (b) from the 3D volume (a) show detection of gold particles. The 50% Au isoconcentration surfaces were constructed to trap the particles in the 3D space (c).

Figure 5.9. A 3D image of a PAPO/AuNP film from an atom probe test. The reconstructed volume (a) was composed of PAPO fragments (green dots) and gold atoms (red dots). Five slice image of cross-sections (b) from the 3D volume (a) showed
presence of gold particles. The 50% Au isoconcentration surfaces were constructed to trap the particles in the 3D space (c).

The cross-sectional images show gold particles embedded in the green polymer matrix at different positions. 2D projections of Au atom arrangements from the volume embraced in two 50% Au isosurfaces are given in (Fig. 5.9a and c). The black circles in the images are used to define the detected Au nanoparticles. Fragments from PAPO and some other ions such as Pd and Na are not shown in (c) for clarity.

The images show a volume of $25 \times 25 \times 150$ nm$^3$. As mentioned before, the reconstructions was calculated based on the model for single component metal tips. In the voltage history we found that the evaporation field for the polymer layer was 37.5% of that for Pd substrate based on their evaporation voltage. Thus the true thickness of the film in Fig. 5.9 is likely closer to 56 nm.

**Figure 5.10** show detailed views of the embedded particles. Detailed views of the embedded gold nanoparticles in the 3D reconstructed image. Figure (a) shows a layer of composite layer with encapsulated particles (red dots). A concentration profile (b) was constructed long the black line crossing two particles. The diameters of the particles are found to be 1.6 nm and 1.9 nm respectively. Three particles enclosed in an isosurface are shown in (c). The numbers of Au atoms found in the isosurfaces are 68 (in 2.0 nm particle), 59 (in 1.8 nm particle) and 65 (in 1.6 nm particle). The size distribution in (d) was obtained by sampling 33 particles found in the 3D image. We estimate there are about 85 Au atoms in
a 1.4 nm Nanogold particles. The detection efficient of the atom probe evaporation is about 61%, that is, 61% ions evaporated from the material can be successfully detected by the atom probe.

Figure 5.10. Detailed views of the embedded gold nanoparticles in the 3D reconstructed image. (a) shows a layer of composite layer with trapped particles (red dots). A concentration profile (b) was constructed along the black line crossing two particles. The diameters of the particles are found to be 1.6 nm and 1.9 nm respectively. Three particles enclosed in an isosurface are shown in (c). The numbers of gold atoms contained in each black circle agrees with the calculated numbers. The size distribution
was obtained by sampling 33 particles found in the 3D image. The distribution (d) is close to the one obtained from the TEM image.

probe microscope. Thus a gold particle in the 3D reconstruction images contains approximately 40 ~65 Au atoms. The gold isoconcentration surfaces were constructed based on the 3D dot image to find the presence of particles in the embraced volume. Based on the information, it was found the 9 out of the 17 gold isosurfaces trapped 2~ 4 particles while other 8 included only single particles with Au atom numbers about 40 ~ 69. The multiply particles were found in an isosurfaces based on the number of atoms inside. The resulting particle size distribution was calculated, which was consistent with the distribution obtained from TEM image in Fig. 5.3c. Since there were only trace amount of other ions found in the isosurfaces containing multiple particles, it was believed that slight agglomeration of nonfunctionalized Nanogold particles existed.

Fine structure of materials can be investigated by constructing an inter-atomic distance distribution. The distribution gives the probability of finding any two atoms at a given interatomic distance. It has been used to the determination of the local structure of nanoparticles. In the 3D atom probe images, since the spatial positions of gold atoms are known, it’s easy to directly calculate the distances between pairs of atoms. Here we calculate the distance density function (Fig. 5.11a) of pairs of gold atoms found in the reconstruction image Fig. 5.10c. A fit (the red line) is used to identify the peak. It is found an interatomic distance of 0.11 nm has the highest probability. This value is smaller than the Au-Au atomic spacing in the bulk phase, 0.288 nm. This difference may be caused by the dimension
calibration which was based on pure Pd phase. As a comparison, a distance density
distribution function is simulated from a gold fcc crystal with interatomic spacing of 0.288
nm as shown in Fig. 5.11b. It’s different from the experimental data. It shows sharp peaks at
specific location indicating its periodic atom arrangement in crystal lattices. In gold particles
in APT images do not show similar peaks suggesting that the short range arrangement of
atoms is irregular.

![Distance density distribution graphs](image)

**Figure 5.11.** Inter-atomic distance distribution of the gold atoms. (a) is calculated from
the 3D reconstructed image of PAPO/AuNP composite film. d is the distance between
two gold atoms. The density function is normalized. The distribution is calculated from
192 Au atoms in Fig. 5.10c. A fit curve (the red line) is used to identify the peak.
Distance density distribution in (b) is simulated from a gold fcc crystal with interatomic
spacing of 0.288 nm.

In the 3D image, we did not observe crystal structures in gold particles. The number
of atoms in each particle is very limited as calculated before, which is 45 ~ 60. Unlike in the
TEM images, every atoms present in the crystal lattices, 30 ~ 40% gold atoms are missing in
the atom probe images. With this percentage of vacancies, planes in crystal lattices are hard
to find, especially in a 3D space.
In this section, we demonstrate that using electrodeposited PAPO coatings on sharp metal tips is an effective approach to trap and immobilize suspended nanoparticles in solutions. In atom probe analysis, the polymer layer was evaporated with gold nanoparticles and detected as distinct peaks in the mass spectrum. Based on the experience from the previous analysis of pure polymer coatings, the composite films on metal substrates were successfully resolved in the 3D reconstructed images. The polymer matrix and embedded gold nanoparticles can be distinguished clearly. The sizes of the particles in the 3D images were measured and close to the values obtained from the TEM images. The thin and uniform insulating PAPO films deposited by the self-limiting growth mechanism play an important role in analyzing the nanoscale particles for the first time. The novel sample design shows several advantages such as easy to prepare, easy to trap nanoscale analytes and suitable for variety of new materials including core-shell particles, quantum dots or biomolecules.

5.3.2 PANi encapsulated nanoparticles

In this section, the sample of PANi encapsulated Pt particle is prepared and analyzed by APT. Although it’s harder to prepare thin and uniform coatings from many conducting polymers as presented in Chapter 4 because of overgrowth, we did obtain thin coatings on Pd tips from PANi by an improved electrodeposition procedure. In this section we will attempt to use PANi as supporting layer to encapsulate nanoparticles for atom probe analysis.
Platinum particles will be incorporated into polymer coatings by a different approach, in-situ reduction for sequential atom analysis. The result will be compared to the PAPO/Au system.

We used in situ reduction of Pt from H$_2$PtCl$_6$ solution by pure methanol in pre-coated PANi layers on Pd tips. The preparation procedure is illustrated in Fig. 5.12. Procedure for preparing Pt encapsulated PANi coating on Pd tips. The procedure is consisted of three consecutive steps: (1) electrochemical polymerization of PANI from aqueous aniline solution; (2) wet impregnation of PtCl$_6$-2 into the polymer; (3) in situ reduction of Pt by methanol.

![Diagram](image)

**Figure 5.12.** Procedure for preparing Pt encapsulated PANi coating on Pd tips. The procedure is consisted of three consecutive steps: (1) electrochemical polymerization of PANI from aqueous aniline solution; (2) wet impregnation of PtCl$_6$-2 into the polymer; (3) in situ reduction of Pt by methanol.

A PANI/Pt composite film covered tip was tested by the atom probe microscope. The mass spectrum is given in Fig. 5.13. Groups of peaks separated by 1 (u/e) appear in the low mass region.
Figure 5.13. Mass spectra obtained from a PANI/Pt covered Pd specimen by the atom probe microscope. The sample temperature was 52.3 K. 0.2 nJ laser pulsing energy was adopted to field evaporate the surface atoms.

In its mass spectra (Fig. 5.13) three groups of peaks, \((^{194}\text{Pt}^+, ^{195}\text{Pt}^+, ^{196}\text{Pt}^+, ^{198}\text{Pt}^+\))
\((-^{229}(\text{PtCl})^+, ^{230}(\text{PtCl})^+, ^{231}(\text{PtCl})^+)\) and \((^{264}(\text{PtCl})_2^+, ^{265}(\text{PtCl})_2^+, ^{266}(\text{PtCl})_2^+, ^{268}(\text{PtCl})_2^+)\)
were observed at 194~198, 229~231 and 264~268. Those peaks indicate that Pt atoms were found in the PANI layer. The presence of \((\text{PtCl})^+\) and \((\text{PtCl})^{2+}\) suggest that PtCl\(_6^{2-}\) was only partially reduced by methanol.

After the reconstruction image was established, other analysis were applied to identify the phase boundaries and precipitates. The 90 % Pt isoconcentration surfaces (grey) were calculated and visualized in Fig. 5.14a. Pt clusters were randomly distributed in the volume of PANI fragments. There was basically no observable Pd signal suggesting that ion evaporation has not reached the Pd tip surface. Isosurfaces from the reconstruction image are shown in (Fig. 5.14b). 90% Pd iso surface (upper left), 90% PANI iso surface (upper right), combined image (bottom left) and a Pd lattice spacing measurement (bottom right) are given
Figure 5.14. Three-dimensional reconstruction of data obtained from PANI/Pt covered Pd tip. Green dots represent PANI fragments. Pt atoms are distributed in the PANI network. The iso-concentration surface (90% Pt atom) of Pt clusters was shown blue particles (a). Isosurfaces from the 3D reconstruction image are shown in (b). 90% Pd iso surface (upper left), 90% PANi iso surface (upper right), combined image (bottom left) and a Pd lattice spacing measurement (bottom right) are given respectively. The vertical bar in bottom-left figure is 2 nm.
respectively. The validation of the reconstruction was conducted by comparing the spacing between adjacent crystal planes in reconstructed volume with the well defined values from methods. Trial and error procedure was performed in these two steps to obtain proper reconstruction volume. A direct measure of the spacing is around 0.2 –0.3 nm (Fig. 5.14b bottom right), which is close to the values obtained from TEM images (0.225 nm).

A 3D reconstruction image of the PANi/Pt film is given in Fig. 5.15. The isoconcentration surfaces of 90% (atomic density) Pt atom (blue) were constructed (a). An isosurface of Pt is illustrated in (b). A 3D region enclosed in the green box in (a) is shown(c) with three cross-sectional slices. The polymer is colored in green. The blue spots represent Pt atoms. Analyzed PANi film is about 5 nm thick. From a certain angle of view, the crystal planes can be observed. A cubic region (green box in Fig. 5.15a) in the reconstructed thin layer was chosen for zoom-in analysis. The closed isoconcentration surfaces are used to represent the presence of Pt clusters. A zoom-in view of a Pt cluster is shown in Fig. 5.15b. The Pt clusters’ sizes are about $2 \times 2 \times 3$ nm$^3$, which is consistent with reported results$^{61}$. The cluster was able to be resolved by sorting the local density of Pt atoms. The size of Pt the cluster is estimated about 2 nm by 3 nm.
Figure 5.15. A 3D reconstruction image of the PANi/Pt film. The isoconcentration surfaces of 90% (atomic density) Pt atom (blue) were constructed (a). An isosurface of Pt is illustrated in (b). A 3D region enclosed in the green box in (a) is shown (c) with three cross-sectional slices. The polymer is colored in green. The blue spots represent Pt atoms.

1D atomic concentration profiles in the PANi/Pt film is given in Figure 5.16. The concentrations of Pt and polymer along the black line in the cross-sectional slice of the film (a) were calculated as shown in (b). Unlike the gold nanoparticles observed in the 3D atom probe image of PAPO/gold nanoparticles films where the individual particles can be
observed from the local concentration distribution or even by visual inspection, clear boundaries of individual Pt nanoparticles are usually not clearly defined by the constructed isosurfaces.

Figure 5.16. 1D atomic concentration profiles in the PANi/Pt film. The concentrations of Pt and polymer along the black line in the cross-sectional slice of the film (a) were calculated as shown in (b).

In the mass spectrum of PANi/Pt film, comparable amount of (PtCl)$^+$ and (PtCl)$_2^+$ were found along with Pt$^+$ as shown in Figure 5.17a–c, indicating that H$_2$PtCl$_6$ was only
partially reduced by methanol in the in situ reduction. Therefore some Pt atoms were detected from the precursor residuals instead from metal particles, which interfere with the particle identifications. In the PAPO/Au film, the gold nanoparticles were directly incorporated in the polymer layers in the one-step preparation method. No complex gold containing ion was found in the corresponding mass spectrum. Therefore the gold enriched regions found detected by the atom probe microscope have much clearer interfaces from the polymer matrix.

Figure 5.17. 2D concentration distributions of Pt+, (PtCl)⁺ and (PtCl₂)⁺ in the PANi/Pt film.

In this section we developed a new samples design for analyzing nanoparticles with the atom probe microscope. It is to use electropolymerization of monomers to extract and encapsulate nanoparticles from solutions, forming a thin and uniform coating on the atom probe tip. The nanoparticles can be detected by surface evaporation along with the polymer matrix. In the atom probe analysis, the polymer layers serve as a supporting material to immobilize the particles for stable evaporation of individual atoms in the metal phases. Two types of electrodeposited polymers were investigated including insulating
poly(3-aminophenol) and conducting polyaniline. Metal nanoparticles were encapsulated into the polymer coatings. In the reconstructed images, PAPO/Au coated sample shows individual particles suspending in the polymer matrix, which is consistent with the TEM images. The PANi/Pt shows existence of Pt atoms incorporated in the PANi matrix, but the clear boundaries of nanoparticles were not observed. Based on the results from the analysis of 3D images, PAPO is more suitable to serve as the supporting material to encapsulate analytes. It has several advantages over PANi:

(a) Formation of the insulating coatings is more flexible than more conducting coatings. They can be electropolymerized in a wide range of pH’s \(^{62-64}\). But most of the polyaniline depositions need to be taken place in acidic environments after the monomers dissolving in the low pH solutions \(^{65,66}\). Therefore some of the analytes may not be suitable for co-deposition with PANi from the solutions;

(b) Thickness of the films deposited from insulating polymers is more uniform than the conducting polymers due to their self-limiting growth. The conducting polymers tend to overgrow and form irregular coating layers. The films were found hard to grow on the surfaces with small curvatures such as the apex region of the sharp atom probe tips;

(c) Direct encapsulation of nanoparticles by PAPO is much simpler and can be achieved in the simple step method by co-deposition of the polymer with the particles due to its self-limiting growth. But for conducting polymers, it’s difficult to control the morphology of formed coating layers because of the overgrowth;
(d) Because of its simple deposition procedure in wide pH range, the polymer can be used for analyzing more types of nanoscale analytes. The original structure of the analytes can be preserved in the polymer layers. No additional separation step is needed for the nanoscale particles;

(e) Polyphenol and its derivatives have been attracting increasing interest in protein, enzyme and living cell immobilizations for biosensor developments. Any progress in those studies can be directly used by our proposed sample preparation method. This will be drastically extended the application of the atom probe techniques to fundamentally more important systems.

5.4 Conclusions

In this section, we demonstrate that using electrodeposited polymer coatings on sharp metal tips is an effective approach to trap and immobilize suspended nanoparticles in solutions. Two types of polymer coatings were successfully constructed, including conducting polyaniline and insulating poly(3-aminophenol). In atom probe analysis, the polymer layers were evaporated with metal nanoparticles and detected as distinct peaks in the mass spectrum. Based on the experience from the previous analysis of pure polymer coatings, the composite films on metal substrates were successfully resolved in the 3D reconstructed images. The polymer matrix and embedded gold nanoparticles can be distinguished clearly. The sizes of the particles in the 3D images were measured and close to the values obtained
from the TEM images. The novel sample design shows several advantages such as easy to prepare, easy to trap nanoscale analytes and suitable for variety of new materials including core-shell particles, quantum dots or biomolecules.

By comparing the insulating coatings with conducting coating, the former is found more suitable in the proposed sample preparation method. In the reconstructed images, PAPO/Au coated sample shows individual particles suspending in the polymer matrix, which is consistent with the TEM images. The PANi/Pt shows existence of Pt atoms incorporated in the PANi matrix, but the clear boundaries of nanoparticles were not observed. The insulating polymers have several advantages over the conducting polymers: (a) Formation of the insulating coatings is more flexible than more conducting coatings. They can be electropolymerized in a wide range of pH’s;\(^{62-64}\); (b) Thickness of the films deposited from insulating polymers is more uniform than the conducting polymers due to their self-limiting growth; (c) Direct encapsulation of nanoparticles by PAPO is much simpler and can be achieved in the simple step method by co-deposition of the polymer with the particles due to its self-limiting growth; (d) Because of its simple deposition procedure in wide pH range, the polymer can be used for analyzing more types of nanoscale analytes; (e) Polyphenol and its derivatives have been attracting increasing interest in protein, enzyme and living cell immobilizations for biosensor developments. Any progress in those studies can be directly used by our proposed sample preparation method. This will be drastically extended the application of the atom probe techniques to fundamentally more important systems.
The results has shown that the novel sample design for analyzing nanoscale objects by the atom probe technique is a promising approach to fundamentally extend the application of the technique to more important materials.

5.5 References


(52) Nakabayashi, Y. Amperometric biosensors for sensing of hydrogen peroxide based on electron transfer between horseradish peroxidase and ferrocene as a mediator. Analytical Sciences 2000, 16.


In this chapter, various areas of Cu covered Al surfaces formed by reactive deposition were analyzed by the atom probe microscope. The main goal is to find the relationship between Al surface dissolution in alkaline solution and Cu deposition. From the 3D reconstruction images of Cu covered Al surfaces, it is found that both uniform and discontinuous Cu coatings are formed in different surfaces. Concentration profiles across Al/Cu interfaces are calculated to discover the film compositions. It is found that under uniform Cu layers, concentration of Al oxides is low in the interface regions, while thick Al oxides are always found under scattered Cu coatings. Explanations of the results are proposed: stable Cu layers can only be deposited on Al or Al hydride surfaces. On the other hand, formation of Cu layers protects further dissolution of Al surfaces in alkaline solution. Varieties of coating morphologies found on Cu coated Al surfaces indicate the dynamic dissolution on the metal surfaces.

6.1 Introduction

Alkaline dissolution of aluminum has been studied for years as a corrosion process because of its commercial importance such as in application of aluminum-air batteries, surface cleaning in automotive, aerospace, packaging applications. The studies have shown
that in basic solutions the corrosion–dissolution characteristics of pure aluminum may be affected by electrode kinetics, diffusion and electrode potentials on the surface layers. In theoretical studies, several dissolution reaction mechanisms have been proposed. One of the mechanisms was developed by Macdonald et al. based on investigation of aluminum dissolution reaction in concentrated KOH solutions by electrochemical impedance spectroscopy. In this mechanism, OH ions were believed to be added sequentially to Al to eventually form stable aluminate ions.

\[ \text{Al}^{ss} + \text{OH}^- \longrightarrow \text{Al(OH)}_{ads} + e^- \quad [1] \]
\[ \text{Al(OH)}_{ads} + \text{OH}^- \longrightarrow \text{Al(OH)}_{2,ads} + e^- \quad [2] \]
\[ \text{Al(OH)}_{2,ads} + \text{OH}^- \longrightarrow \text{Al(OH)}_{3,ads} + e^- \quad [3] \]
\[ \text{Al(OH)}_{3,ads} + \text{OH}^- \longrightarrow \text{Al(OH)}_{4,ads} + ss \quad [4] \]
\[ ss + H_2O + e^- \longrightarrow H + OH^- \quad [5] \]
\[ H + H_2O + e^- \longrightarrow H_2 + OH^- + ss \quad [6] \]

A different view was proposed by Perrault based on experimental and theoretical studies on the aluminum water system at various pHs. He suggested that the equilibria of aluminum in contact with deoxygenated aqueous solutions involved probably two hydride forms: AlH$_3$ in alkaline solutions and AlH$_{3+2}$ in acids and neutral solutions. No mechanism of the surface reaction taking place on the aluminum electrode was proposed but he assumed that the hydrides might be involved as a reaction intermediate.

Recently Adhikari and Hebert demonstrated that submicron AlH$_3$ particles were formed as a product of open-circuit dissolution in 1 M NaOH solution at room temperature.
by secondary ion mass spectrometry (SIMS) and atomic force microscope (AFM)\textsuperscript{10-12}. Based on their evidence, they proposed a mechanism of aluminum alkaline dissolution as shown follows:

\[
\begin{align*}
H + H_2O + e^- & \rightarrow H_2 + OH^- \quad [7] \\
Al + 3H & \rightarrow AlH \quad [8] \\
AlH_3 + 7OH^- (aq) & \rightarrow Al(OH)_4^- + 3H_2O(aq) + 6e^- \quad [9]
\end{align*}
\]

The equation [9] suggests that further validation on this mechanism can be conducted via reduction of metal ions. Jiahe and Hebert performed series of experiments to investigate potential surface reactions by reducing Cu\textsuperscript{2+} on aluminum foils in alkaline solutions. At pH 11.75, they found that very thin and compact Cu layers were formed on the aluminum surface. Analysis across Cu/Al interfaces is needed to fully reveal the structural and compositional profiles in the nanoscale. But normal analytical tools can only provide limited information because of some difficulties from this system. Cu reductions on the heterogeneous surfaces will likely result in a variety of coating morphologies across the interfaces. As showed in the AFM experiments, AlH\textsubscript{3} particles about 10 ~ 50 nm diameter formed and dissolved during short period time. Therefore the surface compositions are expected to be non-uniform. Thus, high compositional resolution in nanoscale is required. SIMS has sufficient depth resolution, but its lateral resolution is larger than the feature of interest on the aluminum surfaces. TEM has good resolution on 2D dimensions, but hard to provide detailed compositional information across the interfaces.
Here we report results from analysis on the Cu/Al interface prepared by copper reduction on aluminum surfaces in alkaline solution via a three dimensional local electrode atom probe microscope (LEAP). Atom probe microscopy is a technique with an unparalleled ability to resolve material structures with single-atom sensitivity. It can provide both spatial and compositional information of the volume of interest from a single measurement\textsuperscript{13-15}. In the sample preparation we attempted direct deposition of copper on pre-sharpened aluminum tips under the same conduction as in depositions on aluminum foils. The aluminum tips with 20 ~ 100 nm tip diameters were made by electropolishing. By analyzing a number of copper coated aluminum tips a variety of surface morphologies were retained and resolved.

6.2 Experimental Section

6.2.1 Material and Reagents

Glacial acetic acid (a.c.s., Fisher) and perchloric acid HClO\textsubscript{4}(70%, Fisher) were used as received to prepare electro-polishing fluid. Aluminum wire (0.25 mm diameter, 99.99%) was purchased from Structure Probe, Inc. (West Chester, PA) to make atom probe tips. The electropolishing fluid was prepared by mixing perchloric acid with glacial acetic acid (1:4) for Pd wire etching. All aqueous solutions were prepared in 18 MΩ cm deionized water (NANOPure, Barnstead, Dubuque, IA).
6.2.2 Aluminum Tip Preparation

Aluminum tips used in atom probe microscope were etched by electropolishing with a home-made polishing workstation. Typically two atom probe tips were formed in each polishing process from a piece of 10 mm aluminum wire. Briefly Al wire of 0.25 mm diameter was cut and attached to the positive polar of a DC supplier (Kenwood TMI/Texio PAR36-3, 36V/3A). A ring electrode formed by a piece of platinum wire was used as a counter electrode. The Pt ring electrode was mounted on a Newport 423 motorized linear stage, which was equipped with a stepper motor (Zaber Tech. Inc., T-LA28-N) controlled by a Labview program. Material of the wire submerged in the ring electrode was removed gradually by the applied voltage. A neck region formed in the middle of the wire and became thinner until the wire was fractured by gravity. The ring electrode was refreshed periodically in a Teflon cell filled with 5 ml refresh fluid placed directly under the wire and the ring. The specimens were subsequently rinsed through deionized water, methanol or acetone and stored for copper deposition.

To control the tip radius, the Al tips were pre-run in the atom probe microscope (LEAP 3000X SI, Imago Scientific Instruments) before copper deposition. In the pre-run, the specimen was field evaporated with voltage mode. Pulse fraction \( V_{\text{Pulse}} / V_{\text{DC}} \) was set to 10%. The standing voltage \( V_{\text{DC}} \) was gradually ramped up until the desired evaporation rate achieved. The top layers of tip surfaces were removed by field evaporation. The surface evaporation stopped until clean Al surfaces were reached.
6.2.3 Copper Deposition

Copper deposition on Al tips were performed by Dr. Hebert’s group in Iowa State University. Briefly the Al tips were submerged in 10 ml NaOH solution at pH 11.75 for 2 minutes to allow formation of aluminum hydrides. Then 40 ml 0.5 M CuSO₄ solution at same pH was quickly added. Tips were kept in the solution for additional 5 minutes to allow the copper deposition.

6.2.4 Atom Probe Microscopy

Coated Al tips were analyzed by atom probe microscope after being degassed for 6 hours in vacuum. Laser pulsing was imposed on the specimens to stimulate surface evaporation. The laser pulse frequency was 250 kHz. The laser pulse energy was adjusted in the range of 0.2 ~ 5 nJ. During the test, the standing voltage $V_{DC}$ was adjusted to maintain a stable evaporation rate. The emitted atoms passed through the TOF-MS before being detected by the position-sensitive detector. After the surface evaporation passed the interface between Cu and Al, the experiment was stopped. Each emitted fragment’s chemical identity and projected position on the X-Y coordinates of the detector plate was recorded and stored in a computer file. The IVAS software (Imago) was then used to analyze the data file and reconstruct the 3D image of evaporated volume.
6.3 Results and Discussion

As the first step of constructing Cu/Al interfaces for atom probe analysis, Al tips with diameters less than 150 nm were prepared by a home made electro-polisher. Rough adjustments on tip diameter and shank angle were done by applying additional polishing cycles. More precise control on the tip diameters were conducted through surface evaporation in the LEAP microscope. Since the evaporation voltage is proportional to the tip radius of curvature according to the equation $r_{Al\,tip} = \frac{V_{DC}}{k \times F_{Al}}$, the stop voltage was used to estimate $r_{Al\,tip}$.

Cu depositions in alkaline solution were carried out directly after the pretreatment. Unlike on flat aluminum foils, here Cu layers were deposited on the sharp tips. The target region was in the small area of tip apex. Since no comparable research about thin film formation on highly curved convex surface could be found, the influence of the surface curvature on copper deposition was first investigated. Aluminum tips with various tip diameters were prepared for copper deposition. The coated samples were then tested using the atom probe microscope to examine the morphology of coating layers. A summary on the results of 21 samples is plotted in Fig. 6.1. The individual samples are listed along the horizontal axis and are sorted into two categories: successful Cu coatings presented as filled bars and unsuccessful coatings as blank bars. In atom probe testing, the successful coatings showed Cu peaks in the mass spectrums at mass-to-charge ratios of 63.5 u/e ($Cu^{+2}$ ions) and 32.8 u/e ($Cu^+$ ions), while unsuccessful coatings showed no Cu peaks at all. The heights of
bars were corresponding to the tip radius of curvature. Their tip radiuses were estimated using equation [2 -1],

\[ r_{Al\,tip} = \frac{V_{stop}}{kF_{Al}} \]

with geometric enhancement factor \( k \) equal to 3 and evaporation field \( F_{Al} \) for aluminum equal to 19 V/nm. Eight out of the 21 samples were found to have copper layers on the surfaces. For most of them, their tip radiuses were significantly greater than the other 11 samples without copper coatings. Although a detailed investigation on this relationship was out of the scope of this research, a statistical test on the data in Fig. 6.1 could be used to roughly show the correlation between tip radius and successfulness of copper coating.

Figure 6.1. All samples tested by the atom probe microscope are listed along horizontal axis. Their estimated tip radiiues of curvature are proportional to the height of vertical bars. Samples with successful Cu coating are represented as filled bars; others without successful Cu coatings are represented as blank bars. A horizontal line corresponding to 50 nm radius is drawn in the graph for reference.
This was important for choosing proper tip radius for the following experiments. Here Fisher's exact test was adapted. Three steps were involved: 1) categorize the results of 21 LEAP runs from 21 specimens into two group: \( r_{tip \ curvature} > 50 \text{ nm} \) (9 samples / or runs), and \( r_{tip \ curvature} > 50 \text{ nm} \) (12 samples/ or runs); 2) count the number of tips with/without presence of Cu coating on Al tips in two categories. One group ( > 50 nm) has 7 tips with Cu coating and 2 without; the other group (< 50 nm) has 1 tip with Cu cap and 11 without. After the first two steps, a table was constructed (Table 6.1). In the last step, the p-value for Fisher's exact test was calculated. A P-value of less than 0.002 was obtained. It means based on the data in Fig. 6.1, possibility of unsuccessful coating on a tip of radius greater than 50 nm is less than 0.2%. Although the result shows that larger tip radius is more likely to achieve successful coatings, the evaporation voltage in the atom probe test needs to be higher as well. So tip radius a little greater than 50 nm, or the stop voltage \( V \) about 3000 V was adapted. Cu film on sharp Al tips is hardly found probably because that formed thin Cu coatings are easy to fall off from the substrate due to even slight shrinkage of the film from drying.

Table 6.1. Results of 21 LEAP runs on each Al specimens categorized according to evaporation voltage and presence/absence of Cu coatings.

<table>
<thead>
<tr>
<th>( r_{Al \ tip} )</th>
<th>( \text{Coated} )</th>
<th>( \text{Un-Coated} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 50 nm</td>
<td>1</td>
<td>11</td>
</tr>
<tr>
<td>&gt; 50 nm</td>
<td>7</td>
<td>2</td>
</tr>
</tbody>
</table>
Copper coatings were prepared directly on the pre-cleaned aluminum tips by Dr. Hebert’s group and analyzed by the atom probe microscope as received. A typical process of analysis started from evaporating the surface in an ultra high vacuum chamber at 50 K. Because aluminum oxides were thought to exist on the surfaces, which were nonconductive materials, pulsing laser was used on the tip to induce surface evaporation. A standing voltage $V_{DC}$ was applied on the sample as well to bring the near-surface potential close to the evaporation field. The combination of laser pulsing and $V_{DC}$ was carefully explored to achieve a stable evaporation rate in terms of ions detected per pulse. A voltage history was presented in Fig. 6.2a. The voltage gradually increases along the proceeding of the evaporation. A clear voltage transition in the range of the ion sequence from 120,000 to 200,000 was observed. This indicates the evaporation passing the interface between Cu and Al substrate. The evaporation field of pure Cu (30.0 V/nm) is higher than that of Al (19.0 V/nm). Here we observe that the evaporation voltage in the Cu coating layer is lower the Al substrate. The reason of this discrepancy is that the Cu layer was not fully covering all area of Al surface, therefore small radius of these discontinuous Cu areas cause allows the Cu atoms to be evaporated in a relatively lower voltage. The mass spectrum history is also presented in Fig. 6.2b. From the mass spectrum it becomes clear that in the early stage of evaporation, the majority of detected ions were $\text{Cu}^+$, $\text{CuO}^+$ and $\text{AlO}^-$. In the transition area cycled in Fig. 6.2a&b, no Cu-containing ions are observed. After 200,000 hits, the amount of $\text{AlO}^-$
decreased while large number of Al$^+$ and Al$^{2+}$ ion were detected. Combining information from the voltage and mass spectrum history, the Cu/Al interface can be located.

Figure 6.2. Voltage history (A) and Mass-to-Charge ratio history (B) from an atom probe analysis on a Cu coated Al tip. The ellipse covered regions in the two charts corresponds to the Cu-to-Al interface. As the sample surface was evaporated layer by layer, instant mass spectrum of detected ions were recorded along the ion sequence number. In the Mass-to-Charge ratio history Cu$^+$, CuO$^+$ ions were found in the early stage of evaporation and disappeared after the interface. Al$^+$ ions become predominant after the interface. AlO$^+$ ions existed through the whole experiment but the intensity
Mass spectrums from Al surfaces with different treatments are given in Fig. 6.3a~c. Three mass spectrums were obtained from a clean Al substrate (a), an Al treated in alkaline solution (b) and an Al surface coated by Cu (c) respectively. The ions were identified according to their mass-to-charge ratios. In (a), the clean Al surface only shows $\text{Al}^+$ at 27. In (b), the surface treated in alkaline solution shows some additional ions such as $\text{Al}^{2+}, \text{Al}^{3+}, \text{AlH}_x^+, \text{AlOH}_x^+$ and $\text{H}_x\text{O}^+$, indicating the formation of surface hydrides and oxides. In Fig. 6.3c, various ions can be found. Copper related ions were identified including single atoms Cu$^+$ and their oxides CuO$^+$. Two isotopic peaks for Cu$^+$ ions at 63 and 65 were the major peaks in the high mass region of the mass spectrum. The relative intensities of the two peaks were consistent with their natural abundances. Small amount of CuO$^+$ ions were observed at
Figure 6.3. Mass spectrums from Al surfaces with different treatments. Three mass spectrums were obtained from a clean Al substrate (a), an Al treated in alkaline solution (b) and a Al surface coated by Cu (c) respectively. The last MS (c) includes all the collected ions across the Cu/Al interface. The ions were identified according to their mass-to-charge ratios.
79 and 81, which corresponded to the oxides formed by the two copper isotopes. Their relative intensities were also consistent with Cu isotopes’ natural abundances. Peaks at 43, 44 and 45 were thought to be the ions $\text{AlO}^+$, $(\text{AlOH})^+$ and $(\text{AlOH}_2)^+$ evaporated from aluminum oxides or its hydrates. Since the evaporation was conducted in ultrahigh vacuum, oxygen in these ions should come from oxides instead of recombination of oxygen atoms in gas phase with charged Al ions. For the same reason, hydrogen in $(\text{AlOH})^+$ and $(\text{AlOH}_2)^+$ were thought from aluminum hydrates. Peaks at 9, 13.5 and 27 were assigned to $\text{Al}^{3+}$, $\text{Al}^{2+}$ and $\text{Al}^+$ cations respectively. Peaks at 28 and 29 were thought to be $\text{AlH}^+$ and $\text{AlH}_2^+$. Peaks at 17 ~ 19 were determined as $\text{HO}^+$, $\text{H}_2\text{O}^+$ and $\text{H}_3\text{O}^+$ from hydrates or water molecules adsorbed on the surface. Small amount of $\text{Na}^+$ cations were also found at 23 as residuals from $\text{Na}_2\text{SO}_4$ in copper deposition solution. After assigning the identities to the ions, they were used to reconstruct the analyzed volume.

Three dimensional images of the evaporated volume can be reconstructed based on the ions’ positions and chemical identities. As an example, reconstruction on the aforementioned sample in Fig. 6.2 and 6.3 is briefly explained. The evaporation voltage of (2-1), the radius was calculated equal to 52.5 nm. The half shank angle of the tip was estimated from the voltage evolution angle vs. depth. Based on the tip radius and half shank angle, shape of the tip was determined. Ions then were arranged in the volume according to their lateral positions detected by the position sensitive detector and depth from initial surface by the ion evaporation sequence. In this analysis totally 3,095,159 ions were used. By slightly adjusting
Figure 6.4. Three dimensional dot image (a) and isoconcentration surfaces (b) of the volumetric data sets in Fig. 6.3 are reconstructed. Two dimensional ionic concentration distributions are projected on XY plane, which was perpendicular to tip axial axis (c - h).

about 3500 V at the point the analysis reached to the aluminum substrate was found in the voltage history (Fig. 6.2) and used to estimate the tip initial radius. By applying equation
radius and high shank angle, the atomic density of reconstructed volume was brought close to density of bulk aluminum. The 3D image of samples including Cu layers (orange region) and aluminum substrate (blue region) is presented in Fig. 6.4a.

According to the AFM results in Adhikari’s research, dissolving aluminum surface in alkaline solution was an unstable process involving AlH$_3$ particles about 30 nm forming and bursting in the period of several minutes. So the coating layers on the nanoscale area of aluminum tip apex were expected to be heterogeneous. In order to capture various features, large number of replicate samples was tested by the atom probe microscope. The morphologies of copper layers discovered in the 3D images agreed with this prediction. Both granular copper regions and uniform layers were found in various samples and to be explained in the following content.

First, a typical surface with partially covered copper regions can be found in Fig. 6.4a. The total reconstruction volume was 92748.7 nm$^3$. Cu atoms were colored in orange. Three granular copper regions were observed on the top of aluminum substrate. Some other types of ions were also detected in the surface region. Iso-concentration surfaces for Al and Cu enriched regions were calculated to find phase boundaries and illustrated in Fig. 6.4(b). The three orange isosurfaces embraced copper enriched regions. The blue isosurface corresponded to aluminum substrate. In Fig. 6.4c-h, two dimensional ion concentration distributions are projected on XY plane, which is perpendicular to tip axial. The red color refers to the highest ionic concentration; while the blue color represents the lowest
concentration. O$^+$ and AlO$^+$ are found to be the predominant ions covering the surface. Comparing the 2D profiles of the two ions, one can find that their covered areas coincide with each other. It indicates that they are fragments from the same materials such as aluminum oxides or aluminum hydroxides. Small amount of AlOH$^+$, AlOH$_2^+$ and OH$^+$ are also observed in the area overlapping with O$^+$ and AlO$^+$, suggesting they were ions evaporated from aluminum hydroxides as well. Coincidence of Al and O atoms in the concentration distributions shows the existence of aluminum hydroxides.

Concentration profiles along the depth were also calculated to provide spatial information. Because of the inhomogeneity of the coating layer, five segregated volumes cut from the initial reconstruction were used to generate local depth concentration profiles (Fig. 6.5a). They were defined by colored cubic boxes. The long sides of the boxes were parallel to tip axle with same cross-section areas of 10×10 nm$^2$. Three of them were chosen to include copper granules, while other two were focused in the areas where the Al surface were barely covered Cu. The depth concentration profiles of the five regions are given in Fig. 6.5b–f. The blue, red and green regions all showed copper layers of 3 ~ 3.3 nm thick forming on top of aluminum oxide layers of various thicknesses. The oxide layers are defined as the transitional regions in the depth profiles between pure Cu layers and Al bulk, where significant amount of AlO$^+$ and O$^+$ were observed. Using 1% as cutoff concentrations for AlO$^+$ plus O$^+$ ion distributions, the thicknesses of oxide layers were measured as 7 nm (in Blue box), 5 nm (in Red box) and 7 nm (in Green box). The depth profiles from the Pink and Yellow boxes (in
**Fig. 6.5b & f** didn’t show the presence of copper layer. The film thickness in (b) is 13.8 nm, while that in (f) is only 0.9 nm thick. The large variation in thickness across the surface is consistent with observations from other studies that heterogeneous surfaces were found in dissolution of Al in basic solutions\(^3,5,6,11\). For example, In Adhikari’s studies, they thought the aluminum hydroxides were created from the AlH\(_3\) oxidation. Their AFM results suggested that the AlH\(_3^+\) existed in the form of nanoscale particles. Formation of Cu layers stopped the oxidation and dissolution. Therefore the rough AlH\(_3\) surface resulted in the heterogeneous thickness of oxide layers. In 3D analysis of our sample, although the copper reduction occurred, no direct evidence of existence of aluminum hydrates is found since there was no significant amount of AlH\(_x\) ion detected in the interface region. One possible explanation was thought to be that small amount of AlH\(_3\) ions were instantly oxidized by oxygen decomposed from the aluminum hydroxides during laser induced evaporation. Based on this it is reasonable to hypothesize that if the aluminum hydroxide layer formed in aluminum alkaline solution was thin enough, that is, Cu layers were formed fast enough to protect aluminum surface from further oxidation, aluminum hydrides are possible to be detected in atom probe microscope.
Figure 6.5. Five sub volumes are located in colored cubic boxes for depth concentration profile analysis. The concentration profiles are given in (b - f) for the five regions.

Another surface with copper coating is presented in Figure 6.6. The copper layer on this sample was more uniform than the previous one. The total reconstruction volume was
722,282 nm$^3$. The tip diameter was 61 nm. Comparing to the previous sample, the amount of O$^+$ and AlO$^+$ were much less. The distributions of O$^+$, AlO$^+$, AlOH$^+$ and AlOH$_2^+$ coincided very well, indicating existence of aluminum oxides and hydroxides. In the lower right of 2D projections, there was a Cu enriched area where the concentrations of aluminum oxides and hydroxides were low, suggesting a relative fast Cu deposition occurred to prevent formation of thick hydroxide layer. From the mass spectrum of the experiment, mass-to-charge peaks at 28, 29 and 30 were found which did not appear in the previous example which corresponds to AlH$^+$, AlH$_2^+$ and AlH$_3^+$. The concentration distributions of these ions also matched those of aluminum hydroxides. Their concentrations were all higher in the upper left area while lower in the lower right.

In Figure 6.7, depth concentration profiles from segregated regions similar as in the previous example were calculated. Pink and red cubes enclose the volumes with dense copper layers. Yellow and green ones contain two regions with scarce copper. In the pink region, the copper layer was found about 1.8 nm thick on the top of a 2.4 nm aluminum oxide layer. The oxide layer was thinner than that in the previous example. 5.2 % of AlH$_x$
Figure 6.6. Three dimensional isoconcentration surfaces (a) with a uniform Cu layer. Two dimensional ionic concentration distributions are projected on XY plane, which was perpendicular to tip axial are calculated (b - i).
Figure 6.7. Four sub volumes are located in colored cubic boxes for depth concentration profile analysis. The concentration profiles are given in (b - f) for the five regions.
appeared in the interfacial region. Contrary to this region, the volume in the yellow box was barely covered by copper. The major composition was aluminum oxides or hydroxides, forming a 2.7 nm layer. 10.5 % AlH$_x$ in this layer were also found, consistent with the hypothesis. In the other two regions in red and green box, the concentration profiles were similar with a mix layer of Cu, aluminum hydroxides and hydrides.

According to the surface reaction (9), the aluminum hydride oxidation provides electrons for copper reduction. The depth concentration profiles showed that copper layers were always deposited on the top of aluminum oxide or hydroxide layer. This can be interpreted that Cu$^{2+}$ ions from the alkaline solution did not react with AlH$_3$ directly. AlH$_3$ oxidation occurred more near the aluminum interface. Formation of Cu layers protected further oxidation of AlH$_3$. The second example shows that AlH$_3$ covered under copper coating can be detected by atom probe microscope.

In this section, various areas of Cu covered Al surfaces formed by reactive deposition were analyzed with the atom probe microscope. Heterogeneous coatings were observed which are consistent to the observations in other studies. The nanoscale interface analysis was performed on the 3D reconstructed images obtained from atom probe analysis. Compositional analysis on the transitional layers between the Cu coatings and Al substrates provide direct observations of aluminum hydrates.
6.4 Conclusions

In this chapter, various areas of Cu covered Al surfaces formed by reactive deposition were analyzed with the atom probe microscope. The Cu/Al interfaces were prepared directly on conventional atom probe tips. Influence of tip diameter on successful film deposition was investigated. Statistical conclusion was drawn from Fisher’s exact test on replicate samples that successful copper coatings could be formed on the tips with radius greater than 50 nm. Cu film on sharp Al tips is hardly to form probably because that formed thin Cu coatings are easy to fall off from the substrate due to even slight shrinkage of the film from drying. 3D images of various areas of Cu covered Al surfaces were reconstructed. Partially covered copper films were found on thick and rough aluminum hydroxide layers, while uniform layer appeared on thin hydroxide layers. The thickness variation in aluminum hydroxide layers is consistent with the observations found in other researches that aluminum surfaces in alkaline solution were dissolved along with constant formation and oxidation of rough AlH$_3$ surfaces. AlH$_3$ was observed in thin aluminum hydroxide layers covered by copper, but not in the thick layers. This is because that the formation of Cu layers protected AlH$_3$ from further oxidation.

6.5 References


CHAPTER 7. CONCLUSIONS AND RECOMMENDATIONS

This dissertation demonstrates our research effort dedicating to extend the application of 3DAPT technique to various new materials including nanoscale monolayers, thin films, interfaces and particles for the first time. The first attempts to analysis monolayers, polymers and nanoparticles have been successfully achieved. A new sample configuration have been proposed as using electrodeposited polymers to encapsulate nanoscale analytes and coat conventional atom probe tips. This design enables the technique to image varieties of new materials which can not be analyzed before. The results demonstrate the ability of modern APT technique in the new areas and inspire the future discoveries.

However, the current algorithm for dimension estimation is based on single component material model. The metal substrates are normally used to estimate the dimensions for the analyzed volumes based on the model. But for multiphase samples, especially with organic monolayers and polymeric coatings, whose evaporation fields can be significantly different from metal substrates, the algorithm can cause significantly inaccurate dimension estimations in 3D images as found in the chapter 3, 4 and 5.

Although currently there is no evaporation field data for polymers, we found that it can be estimated from the evaporation voltage. Since the diameters of the samples do not change drastically as observed from the TEM images, the evaporation field of polymer layers are can be found by:
\[ F_{\text{Polymer}} = \frac{F_{\text{metal surface}} V_{\text{Polymer}}}{V_{\text{metal surface}}} \]

In the 3D images reconstructed based on single phase model, the thickness of polymer layers need to be adjusted according to the ratio: \( \frac{F_{\text{Polymer}}}{F_{\text{metal surface}}} \).

Another approach to more accurately reconstruct 3D images of multiphase samples is to use various evaporation field \( F \) for different materials. In our research we have established a method for polymeric material analysis by atom probe tomography. Therefore polymer coating can be used as model system to find the evaporation field \( F \) of organic materials by comparing to metal evaporation voltages as shown in the previous paragraph. New computer software with ability to assigning \( F \)'s to different phases and automatically reconstruct images will greatly increase the accuracy of dimension estimations for all phases.

Alkanethiol monolayers with various molecular lengths can be used to construct standard monolayers to calibrate thickness of organic layers. Since the thickness of the alkanethiol monolayers have been measured by other methods\(^1\text{–}^5\), the values can be used to compare with the thickness obtained from 3D images. This will be a usefully method to calibrate dimensions for ultrathin organic coatings.

The atom probe data contain much more information which has not been fully explored. Besides concentration profiles, 3D reconstruction images, new data analysis algorithms, especially new method for automatically identify periodic structures within the nanocrystals should be developed.
The novel sample design by using uniform polymer coating on metal tips to encapsulate nanoparticles can be used to analyze any nanoscale objects. An interesting system for further investigation will be quantum dots with core-shell structure. These semiconductor nanocrystallites have radii smaller than the bulk exciton bohr radius. They have attracted numerous interests for many applications\textsuperscript{6-8}. Core-shell quantum dots with covercoating nanocrystallites with higher band gap inorganic materials have been found with improved photoluminescence quantum yields.\textsuperscript{7} The thickness and coverage of the shell layers will significantly influence the quantum yield.

The core-shell quantum dots with various sizes and coating morphologies can be encapsulated in polymer coatings for atom probe imaging. Imaging of the spatial and elemental distributions within the core-shell structure with atom probe tomography will provide direct observations on sub-nano scale. The thickness and coverage of the shell layers can be investigated in 3D reconstructed images in real spaces. Some limitations will be also expected. First, because of the current image reconstruction algorithm based on single component materials, dimensional variations will arise in this multi-component material. For example, one of the widely studied quantum dots, CdSe-ZnS is composed of four elements. If careful dimension calibration can be performed based on multiphase systems, the crystal structures of different phases will be seen. Secondly, in mass spectrum analysis, some of the elements will show overlaid peaks. Therefore, careful peak devolutions is needed to accurately identify the detected ions.
For interfacial analysis of copper coated aluminum surfaces, to further investigate the surface reaction, isotope of H such as deuterium can be used to treat the surface. In the studies of this work, the origin of H-related ions is hard to determine in mass spectrum analysis. By tracing the isotope-related ions such as AlD\textsubscript{x}, it’s easier to prove the existence of surface aluminum hydrides.

Reference

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