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Encapsulation method for atom probe tomography analysis of nanoparticles

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ABSTRACT

Open-space nanomaterials are a widespread class of technologically important materials that are generally incompatible with analysis by atom probe tomography (APT) due to issues with specimen preparation, field evaporation and data reconstruction. The feasibility of encapsulating such non-compact matter in a matrix to enable APT measurements is investigated using nanoparticles as an example. Simulations of field evaporation of a void, and the resulting artifacts in ion trajectory, underpin the requirement that no voids remain after encapsulation. The approach is demonstrated by encapsulating Pt nanoparticles in an ZnO:Al matrix created by atomic layer deposition, a growth technique which offers very high surface coverage and conformality. APT measurements of the Pt nanoparticles are correlated with transmission electron microscopy images and numerical simulations in order to evaluate the accuracy of the APT reconstruction.

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1. Introduction

Atom probe tomography (APT) offers near-atomic scale characterization for small volumes, typically on the order of $0.1 \times 0.1 \times 0.1 \mu\text{m}^3$, in a broad variety of materials, ranging from metals to ceramics [1–4]. However, the technique requires a void-free specimen, generally limiting its application to compact, continuous solids. This requirement originates from a number of constraints. The first issue is that the material under examination should be compatible with the requirements for APT specimen preparation. In practical terms this means it should be able to be manipulated using focused-ion beam (FIB) systems [5]. The second principle issue is that the material must be able to withstand the stresses associated with the strong electric fields used during data acquisition. Voids are not only mechanically weak but can act as field and stress concentrators, further exacerbating the problem. Third, even if data were successfully collected from non-continuous material via APT, questions would arise regarding the accuracy of the spatial reconstruction: the resulting non-hemispherical tip shape during measurement may introduce aberrations in the ion trajectory [6].

As a result of the issues mentioned above, only a few successful

attempts have been made in applying APT to porous, granular or free-standing nanostructured materials. This class of non-compact materials will be collectively referred to as open-space nanomaterials (OSNMs). An example of such a material which is industrially critical yet broadly inaccessible to APT analysis is that of catalytic nanoparticles (NPs). In the chemicals industry approximately 85–90% of products are produced through catalytic processes. A typical instance from daily life is the group of precious metals used in catalytic converters in automobiles to help purify exhaust emissions [7]; in order to improve efficiency and reduce the amount of the precious metal used in each vehicle, NPs can be used instead of larger grains. Characterization of these NPs is important because the nanoscale microstructure has a great effect on the properties of such materials.

There are a few notable examples of successes using APT to analyze particle systems such as catalysts [8–13], organic structures [14], or meteoritic nano-diamonds [15]. In some of these recent studies, one of the most promising preparation strategies used was that of encapsulation, whereby the discontinuous material is turned into a semi-continuous structure conducive to standard FIB preparation by embedding it in a matrix. Potential encapsulation methods include any type of thin film deposition such as ion sputter coating, electron beam evaporation or chemical vapor deposition. However, these methods often result in a non-conformal coating that may still leave nano-sized voids in the

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deposited material [16]. Thus the issues presented above may still not be resolved. An additional consideration is that the materials must have good adhesion in order not to fracture or delaminate during field evaporation. FIB-based Pt (or W) deposition is another method that could be considered for encapsulation. The attractiveness of such an approach is that the necessary apparatus is readily available with standard APT preparation techniques. However, this method results in a Pt–Ga–C alloy (or W–Ga–C) [17], which may not be optimal from an adhesion perspective.

In this work we propose a relatively general method for preparation of a discontinuous material into APT specimens and show an example of this method as applied to nanoparticles. The first part of the paper will examine the necessity that the matrix material be void free. The issues with material strength and fracture are largely self-explanatory, but what is subtler is the potential deleterious effect on the reconstruction. This is explored using a simulation of the field evaporation of a specimen containing a nano-scale void to determine the aberrations that occur in the APT reconstruction.

Based on this stipulation to reduce voids, in the second part we then introduce atomic layer deposition (ALD) as a method which has the potential to fulfill the requirement for encapsulation [15]. ALD is a well-established technique that produces high quality films with a highly conformal deposition [18]. Because it has a very high degree of surface coverage and conformality, ALD can fill voids and encapsulate arbitrary shapes. In the second part of this paper we demonstrate the feasibility of this approach by performing APT analysis of encapsulated Pt nanoparticles.

ALD is able to produce a wide range of material types, including oxides, nitrides, and pure metals. As such, in principle, the matrix composition (and thus the evaporation field) may be tailored to suit the material being investigated. In the final part of this work we consider the accuracy and artifacts in the experimental APT data through cross-correlation of the reconstructions with transmission electron microscopy (TEM) images. By returning to the field-evaporation simulation methods used in the first part, we evaluate the consistency between the two methods. This illustrates the importance of having the flexibility to find complementary matrix/OSNM material systems as well as the value of the simulation in providing a tool to judge potential aberrations.

2. Materials and methods

The simulations of field-evaporation were performed using methods described previously [4,19,20]. In order to estimate the degree of aberration in the spatial reconstruction that occurs when a void within a material is field evaporated, we simulated the field evaporation of a 5 nm diameter void within a specimen of single crystal face centered cubic material with a needle radius of 20 nm.

Pt NPs were deposited in an open-load ALD setup at a substrate temperature of 300 °C. Methylcyclopentadienyl trimethyl platinum (MeCpPtMe₃) and oxygen plasma were used as precursors. The pressure of O₂ gas was 0.01 mbar and the plasma power was 100 W. One ALD cycle of Pt consists of MeCpPtMe₃ 5 s/purge 5 s/pump 5 s/O₂ plasma 0.5 s/purge 1 s/pump 3 s [21].

ZnO:Al films were deposited using an Oxford Instruments OpAL ALD reactor at a substrate temperature of 250 °C. Diethyl zinc [DEZ, Zn(C₂H₅)₂] and deionized water vapor were used as precursors for the growth of the ZnO matrix. Similarly, trimethyl-aluminum [TMA, Al₂(CH₃)₃] and deionized water were used as precursors for the growth of Al₂O₃ used as the dopant in the ZnO matrix [22]. The doping level was controlled through the ratio of deposition cycles of each precursor combination per supercycle. In this work 23 ZnO deposition cycles were performed per Al₂O₃ deposition cycle. The resulting atomic fraction Al/(Al+Zn) of the ZnO:Al films is 6.9% as measured by X-ray photoelectron spectroscopy (XPS).

Layers of ALD ZnO:Al were deposited both prior to, and subsequent to, the Pt NP growth. This was done in order to promote overall adhesion in the encapsulated structure, Fig. 1a–c. A multilayer structure was used for the current work that contained six layers of Pt NPs. This was designed to increase experimental efficiency by allowing different NP growth conditions to be evaluated. The layers of Pt NPs were fabricated using 30, 60 and 100 ALD cycles. Each Pt NP layer was separated by 50 nm of ZnO matrix to ensure that the specimen would return to the equilibrium shape between each layer.

Although ALD was used for both the NPs and the matrix, it must be stressed that the Pt NPs were deposited ex-situ in a different ALD reactor than the one used for the ZnO matrix. Other NP deposition techniques or other open space nanomaterials could have been used just as easily. We chose to use ALD Pt because it allowed us to create a range of NP sizes in a controlled manner, as well as being a material system of technological importance

Fig. 1. Schematic showing method of encapsulation of nanoparticles using atomic layer deposition. In (a) an initial layer is deposited onto which the particles are deposited (b). (c) shows the second ALD layer which encapsulates the particles and an optional additional protective cap material (e.g. nickel) is shown in (d). The final structure after focused ion beam milling is shown in (e).

[21,23].

A key feature of our approach is that the deposition is done directly onto a flat-top Si microtip coupon used by the local electrode atom probe (LEAP) [24]. This reduced specimen preparation time by removing the necessity to lift-out a lamella from the wafer surface. After deposition, the sample is immediately ready for annular milling to form the final APT specimens [5,25,26]. In some instances it may be desirable to deposit a sacrificial technical layer (shown as Nickel Cap in Fig. 1d) before sharpening into the shape shown schematically in Fig. 1e. In the case of the current work, extra ZnO was deposited instead of a Ni capping layer, but in practice this layer could be made from a variety of elements or compounds.

Specimens were analyzed in a CAMECA Instruments LEAP® 4000X HR atom probe at a temperature of 25 K, a laser pulse repetition rate of 100 kHz and a detection rate of one ion per 250 laser pulses. The laser wavelength was 355 nm, pulse duration 10 ps and laser energy per pulse was 50 pJ. The atom probe data presented in this work was reconstructed using a shank angle methodology [4,27] with a shank angle of 18°, image compression factor of 1.65, and an initial radius of 18 nm. Isoconcentration surfaces were calculated using voxel size and smoothing parameters of (0.75, 0.75, 0.75) nm and (2.0, 2.0, 2.0) nm, respectively [28].

TEM studies were performed using a JEOL ARM 200 probe corrected TEM, operated at 200 kV. All imaging was done in high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) mode. The cross-sectional TEM sample of the layer of Pt NPs sandwiched by ZnO layers was prepared by the lift-out method using an FEI DualBeam® FIB. This TEM sample was taken from the identical ZnO:Al/Pt stack but on a blank Si substrate deposited at the same time as the APT specimens. The plan view TEM images of the Pt NPs were acquired from Pt deposited on ZnO:Al matrix-covered Si₃N₄ TEM windows.

3. Results and discussion

3.1. Simulation of nano-void field evaporation.

A field evaporation simulation of a 5 nm diameter void contained within a single crystal face centered cubic material was performed and reconstructed in order to estimate the degree of aberrations which results from such a structure. The simulated structure is shown in Fig. 2a. The atoms which border the void region are colored dark in order to differentiate them from the matrix atoms. Reconstruction parameters were chosen by minimizing the error in positions between the known matrix atom positions and the reconstructed positions using a method described previously [29]. This method resulted in reconstruction conditions of: shank angle of 12°, image compression of 1.56, and an initial radius of 23 nm. The results of this reconstruction are presented in Fig. 2b.

Because we know the initial positions of each field evaporated atom, we may compare the final reconstructed position to the initial position to produce an estimate of the positioning error. The root mean square summed value of the *x*, *y*, and *z* error for the reconstruction shown in Fig. 2b is 1.16 nm. Considering that the void only has a 5 nm diameter, such a variation is a significant deviation from the original shape. Nearly all of this error results from atoms bordering the void. As shown in Fig. 2b, these atoms are artificially widened in *x*–*y* near the top of the void and compressed in *x*–*y* at the bottom of the void. For analysis of NPs, structural details that may be investigated are size, shape (e.g. faceting), composition, and surface area. It is therefore clear that any voids need to be minimized or eliminated in order to produce

Fig. 2. (a) Starting point for simulation of a 5 nm diameter void contained within a single crystal face centered cubic material and (b) the reconstructed image after simulation of field evaporation. The darker spots show just the atoms which are on the edges of the void.

optimal data in encapsulated structures.

3.2. APT measurement of Pt NP encapsulated in ALD ZnO

The layer of Pt NPs fabricated using the 30-cycle ALD process described above is shown in cross-sectional view in the HAADF STEM image in Fig. 3a. The lower ZnO layer is characterized by inclined top facets, explaining the variation in vertical position of the NPs in this image. For the particles in this image, the size range is ~1 nm up to ~5 nm diameter. Fig. 3b shows a partially milled specimen containing the layer of NPs (arrows) encapsulated in between two layers of ZnO (labeled with text). Note, that although there are other layers contained in this overall structure, this lower trilayer is the main region of interest for the current study. The final specimen shape, with the layer of Pt NPs positioned in the near apex region of the specimen is shown in Fig. 3c. Three of the 17 specimens run in this study resulted in the layer of NPs being successfully analyzed. Thus our initial yield for the structure is reasonable at better than one out of six. Notably, many minor fractures occurred at the onset of the 90-cycle Pt layer entering the field of view. This layer had complete coverage of the ZnO surface, which often resulted in delamination at the interface. This emphasizes the importance of having material systems with good adhesion.

Due to the supercycle growth mode used to dope the Al into the ZnO, the Al atoms are found not to be homogeneously distributed. Instead, they form a periodic laminar structure which is detected in the atom probe data. The expected spacing of these layers has been calibrated against XPS depth profiles and cross-sectional TEM studies of similar growths [22]. As such, this periodicity provides an internal scale standard by which the *z*-scaling of the APT data reconstruction can be validated, both in the sense of the total depth and also for the consistency of the thickness of each layer.

An atom probe data set containing layers of ZnO (top and

Fig. 3. (a) HAADF STEM image of a cross-sectional TEM sample displaying the Pt nanoparticles fabricated using the 30-cycle ALD process and sandwiched between ZnO layers, (b) a partially prepared and (c) finished APT specimen containing the Pt particles shown in (a). The arrows show the approximate position of the layer of nanoparticles. Note that (b) and (c) have the same scale.

bottom) enclosing a layer of Pt NPs is shown in Fig. 4. Isoconcentration surfaces derived from the reconstructed atom cloud surround volumes with a high Pt concentration, in this case defined as the atomic concentration of Pt divided by the sum of (Zn+O+Al+Pt) equal to 40%. The particles are shown in plan-view at various isoconcentration surface levels in Fig. 5a–d. Some of the particles appear to be interconnected at the low isoconcentration levels and only a few of the particles are approximately spherical in shape. For example, at the 40% isoconcentration level, we see very few nearly spherical particles (arrow in Fig. 5b). At the 30% isoconcentration level, we observe several nearly spherical particles (arrows in Fig. 5a). At the higher isoconcentration levels we observe that there are nearly zero particles remaining with a core of greater than 60 at% Pt.

An estimate of the internal particle composition may be made using a proximity histogram [30]. Using the particle interface at an isoconcentration level of 40% with 0.1 nm bins produces the profile shown in Fig. 6. The maximum Pt level is approximately 70 ± 7 at% and the region of the particles extends over ~ 2.5 nm. The ratio of Zn:O (dotted line is 5 point moving average) is also given in Fig. 6.

Fig. 4. Atom probe data set containing layers of ZnO (top and bottom) enclosing a layer of Pt nanoparticles (isoconcentration surface $\text{Pt}/(\text{Zn} + \text{O} + \text{Al} + \text{Pt}) = 40\%$). The Zn and O matrix atoms are both shown in the same grey color.

3.3. Correlation with TEM and simulation

The isosurfaces shown in Fig. 5 suggest ion trajectory aberrations may have distorted the particle shapes. This is not surprising considering the field difference between Al:ZnO and Pt, as observed from the specimen voltage evolution during the APT measurements. In this case, the voltage that was applied in order to maintain a constant ion detection rate increases rapidly as the Pt-containing regions appear on the detector. This suggests a case of metal particle (high field) within oxide matrix (low field) similar to that recently reported by Devaraj et al. [31].

Another indication of potential trajectory aberrations and ion crossing [6] is the composition of the Pt NPs. The proxigram analysis shows the particle center concentrations are not pure Pt, as would be expected from the growth. However, it cannot be ruled out that diffusion or mixing during the growth could also be responsible for the dilution of the Pt in the core of the NP.

To consider these two possibilities, the ratio of Zn:O can be compared within the matrix and the particle. In the case that diffusion is responsible for the Pt level difference, we would expect that the Zn:O ratio would be different in the matrix and the NP interior because the two elements likely have different diffusion rates inside the Pt NP. On the other hand, if trajectory aberrations are responsible for the apparent presence of Zn and O in the NP then we would expect the ratio between them to be the same in both the NP and the matrix.

Referring to the proxigram in Fig. 6, in the 1 nm region contained between -4 nm and -3 nm from the 40% isosurface (in the matrix) the Zn:O ratio is 2.52 ± 0.05 while for the region contained between 0 and 1 nm (in particle interior) the ratio is very similar (considering the error) at 2.95 ± 0.35 . Thus we propose that trajectory aberrations are responsible for the lack of purity and the non-spherical shape of the NPs in the APT data.

In order to better understand the probability of trajectory overlaps between the Pt NPs, we have simulated field evaporation of a system of particles, using sizes and distributions based on TEM information (plan view) as shown in Fig. 7a. The particles denoted with dashed circles were placed into a matrix where the particle material has an evaporation field that is a factor of two higher than the matrix material. Three particle sizes of 2 nm, 2.5 nm, and 3 nm were simulated.

Fig. 7b shows a reconstruction of the simulated data with the matrix material displayed as small dots and an isoconcentration surface at 40% Pt. Fig. 7c–f shows Pt isoconcentration surfaces of

Fig. 5. Plan view perspective of the layer of nanoparticles at isoconcentration surface levels of (a) 30%, (b) 40%, (c) 50%, and (d) 60%.

Fig. 6. Proximity histogram calculated using the particles shown in Fig. 5b with 0.1-nm bins. The ratio of Zn to O is shown on the right hand axis. Error bars are $\pm$ one standard error.

case is close to the factor of two that was simulated.

For the case of the larger NPs it is difficult to see how we could observe particles that are less than 100% Pt in the center for the case where there is only one particle in the dataset. The higher field material should protrude during field evaporation, as shown in the simulated shapes in Fig. 9, and the local magnification in such a case would project the Pt ions into the matrix, causing mixing at the periphery. However, this case would not project matrix elements in the center of the particle. This suggests that the reason for the observation of less than 100% Pt in the particle centers, both in the experimental and simulated measurements, is trajectory aberrations [32,33] which occur during the field evaporation of matrix material near *other* particles in the dataset. These matrix ions are projected in a way such that they appear to originate inside particles. The shapes presented in Fig. 9 support this conclusion, most obviously those in Fig. 9e–g.

4. Summary and conclusions

This work presents feasibility for processing nanoparticles into atom probe specimens by encapsulation in a matrix material deposited by atomic layer deposition. Simulations of field evaporation establish the need for a void free matrix for obtaining an accurate reconstruction. ALD materials are proposed as a solution for two principle reasons: (i) they provide exceptional coverage, allowing filling of arbitrary shapes, and (ii) they offer a wide range of different films (metal, oxide, and nitride) that have high purity.

30–60%. For comparison to the experimental data in Fig. 6, a proxigram of the simulated data was created and the result is shown in Fig. 8. The data labeled “Particle” in Fig. 8 match well with the Pt data shown in Fig. 6 both in the shape of the profile and in the maximum concentration at the center of the particles (~70%). Thus we propose that the evaporation field difference between the matrix (ZnO:Al) and the Pt NPs in the experimental

Fig. 7. (a) HAADF STEM image of plan view Pt nanoparticles fabricated on ZnO on a TEM window using the 30-cycle ALD process showing nanoparticle distribution (dashed circles) placed into a low evaporation field matrix for simulation of field evaporation, (b) reconstruction of the simulated data with the matrix material as small dots and a 40% Pt isoconcentration surface, (c–f) Pt isoconcentration surfaces of 30–60%.

Fig. 8. Proximity histogram calculated using the particles shown in Fig. 7b with 0.1-nm bins.

The prototype for this approach was shown on Pt NPs, a material used industrially in catalytic chemistry, encapsulated in an Al-doped ZnO film. An entire Si microtip coupon was coated by ALD with the ZnO:Al matrix, followed by a NP layer, and then ZnO:Al again. By directly depositing the NPs onto a microtip coupon, no lamella lift-out and propagation was needed, reducing specimen processing time. The NP/matrix system was then successfully measured by APT. Good fidelity of the ZnO:Al matrix was achieved; the periodic Al distribution from the ALD supercycle growth scheme could be detected [34].

By comparison to high-resolution TEM images of the NPs we found evidence of trajectory aberrations leading to apparent mixing of the matrix into the NP. This was explored further with simulations of field evaporation of particles of high field material in a low field matrix which were based on an example structure provided by the TEM images. The results of these simulations were consistent with the shapes and concentrations obtained in the experimental data.

Although the NP structures appeared distorted by the trajectory aberrations, the current work proved to be a successful

Fig. 9. Field evaporated shapes from a simulated specimen containing the precipitates circled in Fig. 7a. The dashed line in Fig. 7a corresponds to the plane of the specimen shown above. The evaporation field of the precipitate phase is two times that of the matrix phase. Simulated shapes are shown for (a) 150 k, (b) 170 k, (c) 190 k, (d) 210 k, (e) 230 k, (f) 250 k, (g) 270 k, and (h) 290 k ions field evaporated from the original 20 nm radius specimen.

demonstration of the concept of using ALD materials to encapsulate nanoparticles. (Note that encapsulation using ALD may not be effective when coating materials that have *internal* pores.) The next steps to optimize this process are two-fold. Firstly, the simulations should be used to investigate the parameter space to find what degree of field evaporation matching is necessary for different sizes and densities of NPs in order to minimize the aberrations and obtain accurate experimental results. Secondly, a range of matrix materials should be investigated to find those that match different OSNMs. In the case of the current NPs, this could be done by reducing the Al doping in the ZnO to increase the matrix evaporation field or simply by trying a different material from the wide range of materials that ALD can offer.

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