Final Report

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“Development and Applications of Time of Flight Neutron Depth Profiling”

Cornell University (DOE-Prime)

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Abstract

The depth profiles of intentional or intrinsic constituents of a sample provide valuable information for the characterization of materials. For example, the subtle differences in spatial distribution and composition of many chemical species in the near surface region and across interfacial boundaries can significantly alter the electronic and optical properties of materials. A number of analytical techniques for depth profiling have been developed during the last two decades. Neutron Depth Profiling (NDP) is one of the leading analytical techniques. The NDP is a nondestructive near surface technique that utilizes thermal/cold neutron beam to measure the concentration of specific light elements versus their depth in materials. The depth is obtained from the energy loss of protons, alphas or recoil atoms in substrate materials. Since the charged particle energy determination using surface barrier detector is used for NDP, the depth resolution is highly dependent on the detectors and detection instruments. The depth resolutions of a few tens of nm are achieved with available NDP facilities in the world. However, the performance of NDP needs to be improved in order to obtain a few Å depth resolutions.

An experimental investigation of time-of-flight (TOF) method for NDP was proposed for this study. In this study, a timing start signal was obtained from electrons emitted simultaneous with a neutron-induced recoil particle leaving the surface of the sample. The recoils have low energies compared to charged particles and higher masses therefore they have long flight times. The start signal for flight time measurements was obtained from electrons emitted when the recoil atoms leave the surface of the sample. The electrons are accelerated to a microchannel plate detector to obtain a start signal. The recoil atoms are detected with another microchannel plate detector to obtain a stop signal. The same particle generates the subsequent stop signal, whereby the residual energy of the particle is much more precisely determined from the particle flight time than currently obtained by the use of surface barrier detectors. Consequently, this experimental study is greatly improved the depth resolution of light elements in technologically important materials and further our understanding of dopant behavior in materials.

Project Progress History

a) Cornell University

During the period of July 2001 to June 30, 2002 a conventional NDP facility was set-up and tested at Cornell University, the Ward Center for Nuclear Sciences. All of the components of TOF (Time of Flight) electronics were purchased but were not tested due to closure of the Ward Center for Nuclear Sciences. During this period a Master of Science thesis was completed (see attached) and a paper was published in the Transactions of American Nuclear Society, (see attached). Trans. Am. Nucl. Soc., 86 (2002), 248). The PI (Dr. Ünlü) left Cornell and joined the Pennsylvania State University. All of TOF-NDP related equipment was transferred to Penn State. The remaining funds were subcontracted to Penn State to complete this project. During the period of 10/1/02 to 12/31/03 a graduate student (Zhiqiang Li) worked on this project.

a) Pennsylvania State University

A graduate student (Sacit Cetiner) was recruited for this project and he started working with TOF-NDP project in January 2003. In the beginning, the vacuum chamber was put together and the beam port area at the Breazeale Nuclear Reactor at Penn State was rearranged to accommodate the NDP experimental setup. In the meantime, some off-line measurements with several alpha sources were performed to test the integrity and reliability of the overall experimental system. These tests were related to conventional NDP, in which the residual energy of the charged particles is measured. The objective was to reproduce the experimental data collected at Cornell Research Reactor at Ward Center for Nuclear Sciences by Li for his master's thesis. The first on-line experiments were performed in early July 2003. The data had significant noise content and several electrical arrangements were experimented to achieve the best signal-to-noise ratio. In the meantime, the experiments were also repeated with different types of charged particle detectors to achieve the highest quality data. Optimal electrical arrangement and the

selection of the right kind of particle detector presented a very good quality data despite the beam quality at the beam port #4 at the Breazeale Nuclear Reactor. The beam port was designed specifically for radiography/radioscopy experiments and therefore had major drawbacks in the required beam quality setting from the NDP experiments' standpoint.

During the period of May 5, 2002 to May 4, 2003 a temporary collimation system for beam port No 4 was design and built, neutron flux measurement was performed and neutron spectrum was measured using a slow neutron chopper. The slow neutron chopper setup picture and a diagram and measured data compared with Maxwell Boltzman distribution are given in Figure 1-3. After beam neutron flux and spectrum measurement at beam port No 4, a conventional NDP facility was set-up at Radiation Science and Engineering Center at Pennsylvania State University. The testing of conventional NDP was performed at RSEC. A preliminary measured result for Intel Borophosphosilicate wafer is given in Figure 4. Most of the components of TOF (Time of Flight) electronics were purchased previously but were not tested due to closure of the Ward Center for Nuclear Sciences. All of TOF-NDP related equipment was transferred to Penn State.

Figure 1. A picture of Single-Disk-Chopper Neutron Time of Flight Spectrometer

Figure 2. Schematics of Neutron Slow Chopper Setup at RSEC at Penn State

Figure 3. Measured neutron spectrum with slow neutron chopper and calculated Maxwell Boltzman distribution of thermal neutrons.

Figure 4. Boron-10 distribution profiles in Intel Borophosphosilicate wafers measured using conventional NDP facility at Radiation Science and Engineering Center at PSU.

During the period of May 5, 2003 to May 4, 2004 the testing of conventional NDP was completed at the Radiation Science and Engineering Center beam facility at PSU. A layout of the beam facility is shown in Figure 5. Several measurements were carried out using the Penn State NDP facility. The data obtained from PSU-NDP facility

were compared with the measurements performed at UT-Austin NDP facility and Cornell University NDP facility using the same samples. The results of the measurements on

Figure 5. Schematic layout of Penn State Breazeale Nuclear Reactor Beam Port #4.

implanted and borophosphosilicate glass wafers are given Figures 6-10, and shows good agreement with these measured data as well as computational results. As the semiconductor device sizes get smaller, the need for proper analysis techniques becomes an important challenge. The devices will have dopants implanted at very low energies with total depth around 200 Å. Other analytical techniques such as SIMS are not capable of measuring such small thicknesses. Time-of-flight NDP, a new approach to NDP, seems to be promising to overcome the inherent resolution issue in the conventional NDP, and may become an analytical technique to fulfill this demand. The premise is based on the fact that the time measurements can be made with far better resolution. The use of MCP detectors will eliminate the straggling issue in semiconductor detectors. The depth resolution for TOF-NDP is expected to be 5-10 times better than that of the

conventional NDP. A resolution of this magnitude will become an essential tool for semiconductor industry, where high-precision measurements are of paramount importance, in particular for quality assurance/control (QA/QC) purposes. All equipment including MCP's and electronics purchased, sample holder, detector holders and electron steering device designed and built.

Figure 6. Penn State NDP measurement of the energy spectrum of particles emitted by the neutron-boron reaction.

Figure 7. Alpha particle spectrum expanded from Figure 6.

Figure 8. Boron density profile for a borophosphosilicate glass (BPSG) sample

Figure 9. Alpha peaks from the neutron B-10 reaction in a 120-keV B-10 implanted silicon wafer

Figure 10. Comparison of different analytical techniques and simulations for 120-keV B-10 implanted silicon wafer.

The TOF-NDP system involved multichannel plates (MCP) for charged particle and electron detection unlike the conventional NDP systems where usually silicon surface barrier or, as in our case, silicon PIN photodiodes were used. We decided to go with lower quality MCP in the earlier stages of the experimentation, and leave the assembled MCP's purchased from Hamamatsu for ultimate use in the experiments. Gregory R. Downing, the project consultant, provided us three MCP's in bare forms. We designed and manufactured the assemblies for these bare MCP's and tested them. The 3D CAD model is shown in Figure 11.

Figure 11. Assembly designed for 24-mm single MCP's

A schematic of PSU TOF NDP target chamber is shown in Figure 12. Trajectories of electrons and charged particles calculated, and tested experimentally with a Po-210 source. During the period of May 5, 2003 to May 04, 2004, an invited paper was prepared for the American Nuclear Society Annual meeting at Pittsburgh, PA (paper was presented on June 13-17, 2004 and published in Trans. American Nuclear Society, 90, 311 (2004)). Another invited paper was submitted to 11th International Conference on Modern Trends in Activation Analysis at University of Surrey, Gilford, England (paper was presented during the conference on June 20 –25, 2004 and accepted for publication

in the Journal of Radioanalytical and Nuclear Chemistry).

Figure 12. Cross sectional view of the time of flight experimental setup

Because of the space and time considerations at the beam port, early TOF-NDP measurements was performed off-line with a test sample that emulates a depth profile of a charged particle emitter. We found that polonium undergoes spontaneous surface deposition with silver. This was used in the early testing of the experimental setup. Once the proper operation of the system was proved, the same experiments were performed with conventional-NDP technique, which is based on energy measurement. The same measurements were repeated with TOF-NDP. For the final sets of measurements we will show the uniqueness of the TOF technique by performing the depth measurement of a device featuring ultra-shallow junction technology.

Specific Contributions for the Advancement of NDP Technique

- **NDP Software and LabVIEW Integration: NDP-LabVIEW**

LabVIEW has become the *de facto* standard academic and industrial graphical programming environment. Not only is it well-known as a suitable and user friendly graphics environment, but it is also a comprehensive mathematical and signal analysis tool. The extension toolboxes add the liberty of accessing and benefiting LAPACK and BLAS libraries just like using them from a conventional structural programming language. Availability of direct link libraries allow for code integration across different coding platforms.

NDP software written by Zhiqiang Li at Cornell University incorporated a user interface that alleviated file handling and data processing. However it did not employ any post processing on the output of the data neither did it have the capability to generate a plot once the data is analyzed.

Sacit Cetiner, a graduate student at PSU started rearranging Li's C++ code to make it compatible with the LabVIEW. The *main()* interface of Li's code was redesigned to be embedded into a LabVIEW interface as a *Code Interface Node* or a *Call Library Function Node*. The execution experience showed that Call Library Function Node is easier to use and less prone to crashing in case of a user error. The algorithm related to the calculation of the NDP remained intact; only the references to those functions were redesigned.

Figure 13 shows the output of the execution of a sample NDP experiment. The files destinations are supplied with ease through the graphical interface and execution options are selectable via intuitive buttons or switches. The tabbed improves the user perception of even a new starter for NDP. The spectrum analysis is presented in order from left to right: First number of counts vs channel number is given in the first tab, followed by the counts vs energy tab, which only

applies the proper calibration to channels. Then the region of interest (ROI) is zoomed in and the same previous information is given for that particular energy range. The last tab displays the output of the NDP software execution, concentration vs depth, which is the final product of the NDP analysis provided that a proper standard dose is supplied.

Figure 13. LabVIEW user interface for NDP software

The software is also a part of the development efforts that look into updating the NDP software in order to make it compatible with the new releases of stopping power tables. This effort will be explained in the next item in further detail.

One of the nice things of the LabVIEW integration is the capability of dynamic data processing and display. The spectrum can be exported to NDP-LabVIEW without interrupting the data acquisition and the NDP analysis can be performed *in situ*. This will allow the experimenter to observe as the data progress during the experiment.

- **NDP Software Update**

Li's NDP software is a very well written package with an easy-to-use user interface. However, when he authored the code in 2002, he did not have access to the latest releases of the SRIM/TRIM software. The latest releases, namely 2000 and particularly 2003, come with significant corrections in the stopping power coefficients. Dr. Ziegler also bundles previously separate data tables for proton, helium and heavy ions into one single data file. He explains in his web site (<http://www.srim.org>) that he will continue on this path providing the data tables.

The update of the tables and fine tuning of the stopping coefficient parameters significantly improve the analytical estimates of stopping powers and Monte Carlo ion simulations. It has been raised in a number of paper articles that there is a noticeable mismatch between the experimental measurements and TRIM simulations for deeper depths. These latest releases seem to close this gap to some extent.

Instead of parsing these tables and converting them into the format that the NDP software requires, it is easier to redesign the stream handling of the code to allow for direct access to the data tables. As of now, the latest data table release from

Ziegler is of 2003, and we made the NDP software compatible with this release retrospectively.

- **TOF-NDP Simulation with MATLAB**

This simulation provides a methodology for fine tuning the experimental settings and layout rather than finding the correct values by brute-force.

Figure 14 displays the first sequence of the simulation. The simulation graphically displays the progression of the ions and electrons based on the electric field applied between the sample and the electro-mesh sieve, and the magnetic field. There is an optimal arrangement based on these parameters and this optimality can be achieved by running the simulation without having to find it by trial and error.

The simulation also gives the time that passes between the electron strike on the start detector and the ion strike on the stop detector.

Figure 14. A sequence from the MATLAB simulation

- **Adoption of Maximum Entropy (MaxEnt) Reconstruction Algorithm**

Maximum entropy data analysis method arises in the context of making inferences about *positive* and *additive* distributions. The energy distribution of charged particles emitted following a capture reaction from a sample bombarded with neutrons falls into this category, therefore making it a suitable application for MaxEnt algorithm.

The objective of any reconstruction algorithm is to reveal the actual physical phenomenon, which is usually blurred or in general filtered out by intermediate processes. This is also the case for the transport of charged particles emitted following the neutron absorption. The energy loss of particles, which is calculated under certain assumptions, is disturbed by other mechanisms such as energy straggling, system noise, multiple small angle scattering, etc. These disturbances affect the final energy distribution of the particles. In the case of NDP, boron concentration as a function of depth in the sample is resolved from the observed energy spectrum and the transition matrix. This is an example of a linear inverse problem. Inverse problems are famous for their ill-posed properties in their solutions in that different solutions might predict the same data equally well depending on the regularization method used.

It was pointed out by Shannon^{*} that any probability is associated a well-defined information content, which should be identified as (minus) its entropy. The algebraic form of this entropy is

$$S = - \sum_i p_i \log p_i \quad (1)$$

^{*} C. E. Shannon, A Mathematical Theory of Communication, *Bell System Technical Journal*, **27**, pp. 379-423 and 623-656.

for a discrete set of probabilities $\{p_i\}$, $\sum_i p_i = 1$. It has been shown that this is, apart from the arbitrary base of the logarithm, a unique measure satisfying the axioms one assigns to additive information. In maximum entropy regularization, the following nonlinear function is used as side constraint:

$$\Omega(\mathbf{x}) = \sum_{i=1}^n x_i \log(\omega_i x_i) \quad (2)$$

where x_i are the positive elements of the vector $\mathbf{x}$, and $\omega_1, \dots, \omega_n$ are n weights.

Figure 15. (I) Original spectrum (II) Noise that will be introduced to the original data (III) Inverse-Fourier reconstruction of the noisy data (IV) MaxEnt reconstruction of the noisy data

The process of slowing down of ions in the medium is also a stochastic event, and therefore, according to the statistical theory, it might as well be thought that the process itself has entropy. The solution that has the highest entropy is then the one with the highest information content, and less non-process related data. This is equivalent to do “data fitting” that has the highest entropy.

The number of counts in an NDP spectrum –in general any spectrum- is always a positive quantity. The number of counts vs energy corresponds to the vector $\mathbf{x}$ in (2).

Figure 15 gives an application of the MaxEnt algorithm by doing comparison between a reconstructed data by inverse Fourier transform and the one by maximum entropy. Top-left spectrum is the original spectrum, and top-right is the noise that is introduced into the distribution. Bottom-left figure is the inverse-Fourier deconvolution of the noised original data. It reveals the two peaks in the original distribution, but also gives other spurious artifacts that were not included in the original data. However, as seen in the bottom-right, reconstruction using maximum entropy priors (MaxEnt) gives a very close distribution to the original one.

MaxEnt algorithm provides an optimal criterion for selecting a positive image when faced with incomplete or noisy data. The MaxEnt choice can be interpreted as the maximally non-committing solution that is consistent with the data. As such, it tends to be less noisy and has fewer artifacts than the conventional methods, thus making it easier to interpret the results.

Summary

In neutron depth profiling, the data is the energy spectrum of the residual energies of charged particles emitted from the sample following the reaction with neutrons. The energy continuum or continua in the spectrum are the result of energy loss of ions as they travel towards the surface of the sample. If the medium in which charged particles move is known *a priori* then from the stopping power correlations one can find the location at which each particle is originated, which in turn shows the locus of the parent nucleus. The significance of NDP is the absolute information contained in the energy loss mechanism. There is no need for calibration, as needed in other ion beam analysis techniques such as SIMS, and therefore NDP has been used as the standard technique for calibration.

The testing of the MCP assemblies with defected MCP's provided by Gregory R. Downing is complete. We are now in the process of testing MCP's that will give a standard output at a given supply voltage. The Hamamatsu MCP's that are purchased for this project are also being used for the TOF-NDP measurements. The initial results obtained are satisfactory. The final results will be presented in a PhD dissertation and will be published in refereed journals.

PRESENTATIONS

Several presentation are given related to this project by the PI, Dr. Kenan Ünlü, and his graduate students Zhiqiang Li at Cornell University, and Sacit Cetiner at Pennsylvania Sate University. Some of the presentations are listed below:

K. Ünlü, and R.G. Downing, "*Development of Time-of Flight Neutron Depth Profiling at Cornell,*" 2001 American Nuclear Society Annual Meeting, Milwaukee, Wisconsin, June 17-21, 2001

K. Ünlü, *Applications of Neutron Beam Techniques in Science and Engineering*, (Invited Speaker), The Ohio State University, Nuclear Engineering Seminar, November, 2001, Columbus, Ohio.

K. Ünlü, *Applications of Neutron Beam Techniques in Materials Research*, (Invited Speaker), The University of Texas at Austin, Nuclear Engineering Seminar, November, 2001, Austin, Texas.

K. Ünlü, *Applications of Neutron Beam Techniques in Materials Research*, (Invited Speaker), The Pennsylvania State University, Nuclear Engineering Colloquium, January, 2002, University Park, Pennsylvania

K. Ünlü, *Neutron Depth Profiling and its Applications in Materials Science*. (Invited Speaker), The University of Texas at Austin, Nuclear Engineering Seminar, January, 2002, Austin, Texas.

Z. Li, *Progress on the Development of Time-of-Flight Neutron Depth Profiling at Cornell*,” 2002 American Nuclear Society Annual Meeting, Hollywood, Florida, June (2002)

S. M. Cetiner, “*Development of time-of-flight neutron depth profiling at the Pennsylvania State University*,” 2004 American Nuclear Society Annual Meeting, Pittsburgh, Pennsylvania, June (2004).

K. Ünlü, “*Development of time-of-flight neutron depth profiling at the Pennsylvania State University*,” (Invited Speaker), 11th International Conference on “Modern Trends in Activation Analysis”, June 20 25, University of Surrey, Gilford, UK (2004)

PUBLICATIONS

K. Ünlü, and R.G. Downing, “*Development of Time-of Flight Neutron Depth Profiling at Cornell*,” Trans. Am. Nucl. Soc., 84, 82 (2001).

Z. Li, and K. Ünlü, “*Progress on the Development of Time-of-Flight Neutron Depth Profiling at Cornell*,” Trans. Am. Nucl. Soc., 85, 248 (2002).

S. M. Cetiner, K. Ünlü, G. Downing, “*Development of time-of-flight neutron depth profiling at the Pennsylvania State University*,” Trans. Am. Nucl. Soc., 90, 311 (2004).

S. M. Cetiner, K. Ünlü, G. Downing, “*Development of time-of-flight neutron depth profiling at the Pennsylvania State University*,” Presented at the 11th International Conference on “Modern Trends in Activation Analysis”, June 20 25, University of Surrey, Gilford, UK (2004), and accepted for publication in the Journal of Radioanalytical and Nuclear Chemistry.

K. Ünlü, S. M. Cetiner, Jared Hoover, “Neutron Depth Profiling (NDP) Studies at the Penn State University Breazeale Nuclear Reactor”, Pennsylvania State University, Radiation Science and Engineering Center, 48th Annual Progress Report, December 2003

K. Ünlü, S. M. Cetiner, “Time-of-Flight Neutron Depth Profiling (TOF-NDP) at the Penn State University Breazeale Nuclear Reactor”, Pennsylvania State University, Radiation Science and Engineering Center, 49th Annual Progress Report, December 2004

M.Sc. Thesis: Zhiqiang Li, “Development of Conventional and Time-of-Flight Neutron Depth Profiling at Cornell”, Cornell University, Graduate Field of Nuclear Science and Engineering, Ithaca, NY, August, 2002

Ph D. Thesis: Sacit M. Cetiner, “Development and Applications of Time-of-Flight Neutron Depth Profiling”, Pennsylvania State University, The Department of Mechanical and Nuclear Engineering, University Park, PA (in progress)

ATTACHMENTS

- 1) ANS Paper (Trans. Am. Nucl. Soc., 84, 82 (2001))**
- 2) ANS Paper (Trans. Am. Nucl. Soc., 85, 248 (2002))**
- 3) MSc. Thesis, Zhiqiang Li, Cornell University (2002)**
- 4) Radiation Science and Engineering Center, 48th Annual Progress Report, December 2003**
- 5) ANS Paper (Trans. Am. Nucl. Soc., 90, 311 (2004))**
- 6) Radiation Science and Engineering Center, 49th Annual Progress Report, December 2004**
- 7) Journal of Radioanalytical and Nuclear Chemistry paper (accepted for publication)**