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NEAR-SURFACE ELEMENTAL ANALYSIS OF SOLIDS BY NEUTRON DEPTH PROFILING

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Abstract

Neutron Depth Profiling (NDP) is an analytical nuclear technique for the determination of elemental mass as a function of depth into a sample's surface. It is suitable for characterizing a few select elements in most solid materials to depths of micrometers and with the resolution of 10's of nanometers. The most commonly measured elements are helium, lithium, boron and nitrogen. Applications include the study of implanted boron in semiconductor substrates, measurement of helium embedded into first shielding wall alloys/metals used in fusion reactors, lithium diffusion through all solid-state thin-film batteries, and nitrogen penetration into corroded building materials. A brief review of past NDP research as well as NDP instrumentation development both at NIST and other national and international NDP research facilities will be presented. Future research opportunities and current development projects will be discussed.

Introduction

Neutron depth profiling (NDP) is a non-destructive, analytical nuclear technique for the determination of elemental mass as a function of its depth in a sample's surface. The method on which NDP is based was first described in 1972 by Zeigler *et al.* to study B impurities in solids [1]. It was advanced to its current state by Biersack and coworkers (Institute Laue-Langevin, Grenoble) in the 70's and 80's [2, 3]. Currently, there are more than seven (7) NDP instruments in operation around the globe [4], which are maintained by neutron science user facilities.

Methods

The key reaction of NDP is neutron capture by a nucleus to form an unstable, compound nucleus, which will undergo an exoergic charged particle reaction (Figure 1). The reaction products are either an alpha particle or a proton, and a recoiling nucleus. The emitted recoil particles have distinct initial energies - which are indicators of their parent nucleus. As the energetic particles move through the solid they will predominately lose energy as the result of interactions with electrons in the material. The rate of energy loss per unit distance from the particle is a function of the elemental composition and volumetric density of the material, and it is determined by the material's characteristic stopping power. The difference in the initial energy of the charged particles and their final energies as they exit the solid is directly related to the depth of the reacted nucleus from which the particles originated. The relationship between origin depth and measured energy of the particle can be expressed as:

$$x = \int_{E_f}^{E_i} \frac{dE}{S(E)} \quad (1)$$

Where x is the path length traveled by the particle through the solid, E_i is the initial energy of the particle, E_f is the energy of the particle upon exiting the solid, and $S(E)$ is the stopping power of the material.

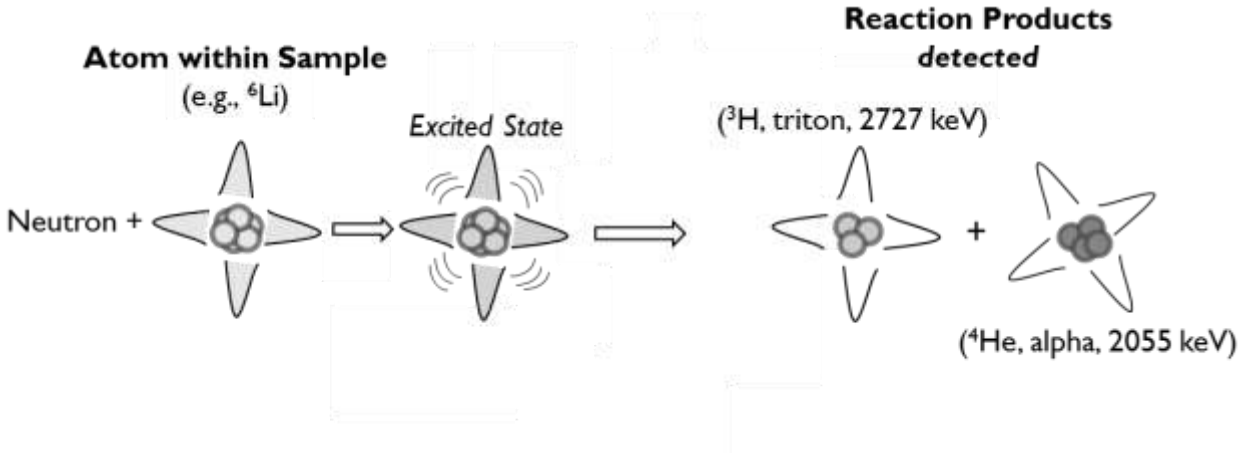

Figure 1. Nuclear reaction for NDP. Depicted example is the reaction of a neutron (n) with ^{6}Li.

Applications

There are only a few select isotopes for which this reaction can be used to measure depth profiles in the near-surface of solids; the most common of which are ^{3}He, ^{6}Li, ^{10}B, and ^{14}N. Other isotopes which have been studied include ^{17}O, ^{22}Na, and ^{7}Be. Much of the early research using NDP was on ^{10}B (^{10}B(n,α)^{7}Li) in semiconductors and metals [5]. ^{10}B is the isotope of boron measured by NDP, which has a very large thermal neutron cross-section (3400 and 241 barns for its two branching reactions), and is 19.9% naturally abundant [6]. NDP has also been utilized to measure B distribution in glasses [7, 8], as well as boron bearing carbides [9].

Li, like B, is another popular element measured by NDP. This is due, in part, to the relative insensitivity of other techniques (particularly those which are x-ray based) to Li. ^{6}Li is the isotope measured by NDP, with a relatively large thermal neutron cross-section (941 barns), and is 7.59% naturally abundant [6]. In recent years the measurement of Li distribution in Li-ion battery materials by NDP has dominated NDP research. *Ex-situ (for examples see* [10, 11]), *in-situ* (for example see [12]), and *in-operando* (for example see [13]) studies of Li diffusion through battery materials and whole cells have been completed by NDP. NDP results coupled with other materials characterization and electrochemical techniques has enabled determination of Li transport numbers through solid-state cells [14], Li diffusion coefficients [15], effect of manufacturing parameters on cell stability and performance (see Figure 2), and to determine the feasibility of novel battery materials [16, 17]. Multi-dimensional mapping of Li in battery electrodes has been achieved within the last decade [18], and there is much anticipation of its continued development. Additionally, advances in lateral spatial mapping of Li in solids have been made using multipixel detectors originally designed for use at CERN [19]. Materials in

which Li profiles have been measured by NDP include ceramics [20], optical wave guides, polymers, and glasses [21].

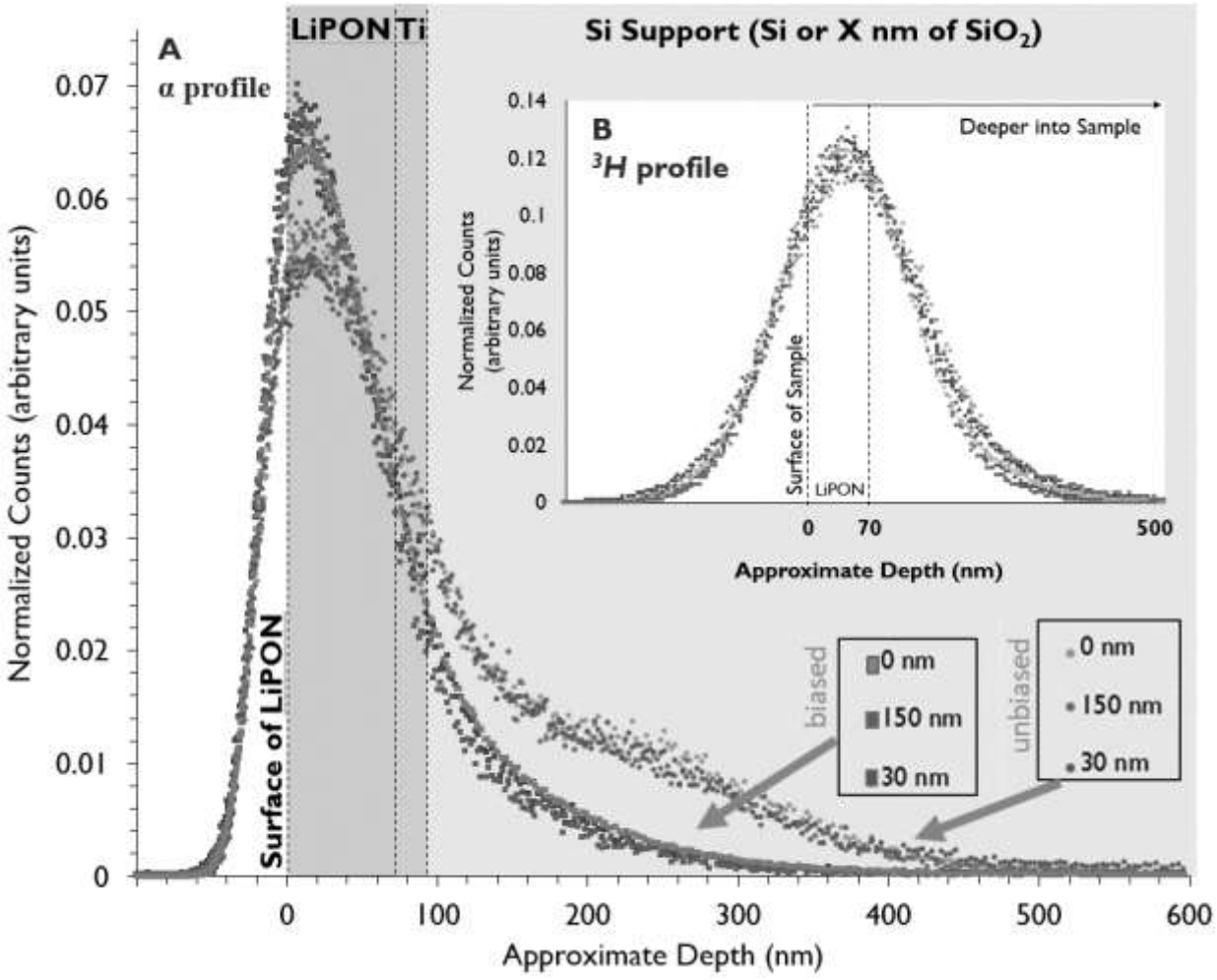

Figure 2. ^{6}Li neutron depth profile collected on a series of solid-state battery cells manufactured under different sputtering conditions (electrically biased and unbiased). NDP allowed for measurement of Li out-diffusion from the cell constructed with a glassy electrolyte (LiPON) as a function of manufacturing and post-processing parameters. Data collected on NIST-NDP instrument.

^{3}He research by NDP has focused on the measurements of implantation profiles of the isotope in alloys and metals. In the late 80's ^{3}He implantation into nickel and amorphous nickel materials was used to understand the microscopic structure and diffusion characteristics through solids[22]. Recently, ^{3}He profiling experiments have been completed for the investigation of shield walls planned for use in next generation fusion reactors. A significant challenge facing the long-term operation of test fusion reactors is the durability of plasma-facing materials and components to intense neutron/neutral/ion particle bombardment and implantation [23]. Tritium is one such erosive particle, and it is known to cause surface blistering and spallation due to entrapment in surface of metals and alloys. ^{3}He is the daughter product of tritium beta decay (½

life of 12.32 years). When tritium is implanted by plasma into the materials its penetration depth and blistering/exposure rates can be measured once it decays to the NDP-detectable ^{3}He ($^{3}He(n,p)^{3}H$) [24]. Similar irradiation damage by helium has been recently measured in $MgAl_2O_4$ crystals, which is a possible matrix to be used for the transmutation and storage of americium [25].

Implantation of ^{14}N into metals has also been investigated by NDP. Over the last few decades there has been considerable interest in the nitride coatings and implantation of nitrogen into metals as means of forming corrosion resistant surface layers, and into semi-conductors and polymers for electronic applications. Fink and co-workers determined through their NDP studies of ^{14}N doped into metals and alloys at high fluence rates that the isotope would diffuse through Mg and Al at room temperature directly following implantation, and through other metals at greater time lengths (0.5 to 4 years) [26]. Of the materials studied, only Cu, Si, and W retained a small percentage of the implanted N over time, while all other materials (Be, Al, Ni, stainless steel, Ta, and Cd) lost all implanted N by diffusion. Other areas of research where ^{14}N NDP may be applicable include sensors and biotechnology [27], as well as archaeometry, and materials corrosion.

Instrument Variations

Sample preparation and NDP measurements are relatively straight forward for the investigation of isotopic profiles in solids. Analysis time is statistically dependent upon the neutron fluence rate and the analyte concentration within the depth interval of charged particle escape from the surface. That is, profile depth resolution is largely a function of analysis time, neutron fluence rate, and mass fraction of the analyte.

The sample should have a relatively smooth surface over the area to be analyzed. The area is not required to have a regular perimeter as an aperture can be customized to fit the shape and area of the surface. The mass fraction of the analyte is determined by analyzing a well-characterized standard using the same aperture and taking a ratio of the known mass to the unknown sample. Calculations are normalized for run time and for total neutron fluence using a neutron monitor simultaneously with the sample analysis. Time dependent measurements are possible by obtaining a series of spectra at appropriate intervals.

All measurements are obtained in an evacuated chamber. The vacuum is needed to ensure that charged particles emerging from the sample surface do not lose additional energy as they travel between the sample surface and the charged particle detector. All NDP instruments are custom built and no two systems are designed the same. Typically, they are designed to best function at the neutron beam line being used. The NDP system in use at NIST is shown in Figure 3. The beam exits the neutron guide at the far right. Neutrons pass a short distance in air and enters the NDP instrument through a thin aluminum window. The beam passes through the chamber containing the sample and exits the instrument through a thin aluminum window. Finally, the residual neutrons continue into a beam absorber at the far left as an aluminum encased box containing lithium and boron rich materials to stop the neutrons and lead shielding to block any gamma component.

Samples are introduced through the lid at the top of the chamber when the system is at atmospheric pressure. There are numerous ports that radiate from the sides and bottom of the stainless-steel chamber. These ports serve to attach vacuum lines, vacuum sensors, up to air values, and electrical connections for the detectors, motion controllers to the sample and detectors, and any electrical connections required for sample environment controls. These environmental controls could dynamically charge and discharge battery systems, heat or cool the sample, attach to thermocouples, translate the sample through the beam, or any variety of research control needs. [28-31]

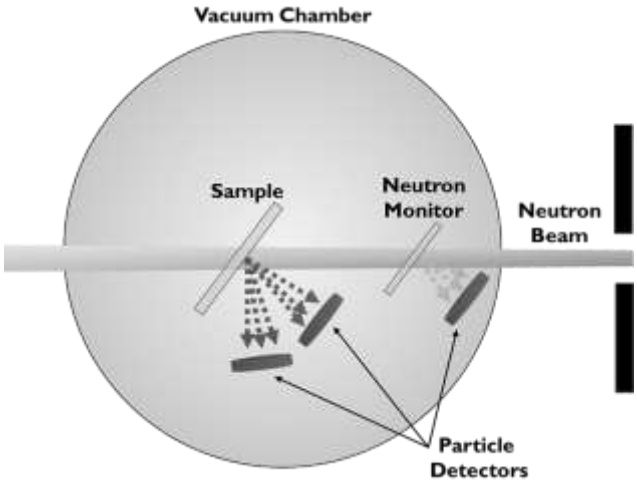

Figure 3. Diagram depicting the inside of the NDP vacuum chamber. All NDP instruments nominally contain the same functionality. The neutron beam traverses the vacuum chamber intersecting the sample mounted near the center of the system. A sample will typically set at an angle to the incoming beam and directly face a charged particle detector placed several centimeters from the sample surface and away from the neutron beam. In the NIST NDP system a neutron beam monitor sits at entrance to the chamber; however other facilities can have the monitor outside the front of the chamber.

Samples are mounted to a removeable holder that can be reproducibly located in the chamber for comparison to other samples, controls, blanks, and standards. A custom-cut aperture is fixed to the sample holder and all of the sample is masked except the area to be analyzed. Neutrons pass through both the masked area and the aperture but the induced charged particles can only pass through the aperture opening to the detector. The charged particles reaching the detector, or detectors, do so with a small angular spread out of the sample such that particles from equal sample depth travel the same distance through the sample.

A variety of charged particle detectors have been used in NDP systems. The silicon surface-barrier detector (SSB) exhibits the best combination of simplicity, energy resolution, and minimal background from gamma-ray, x-ray, and other non-signal sources. Other systems include PIN, ion implanted, time-of-flight, and pixelated detectors. PIN detectors are becoming the most widely used detector. They are inexpensive relative to the SSB detectors and have

comparable energy resolution but are susceptible to considerable spectral noise that starts around 1400 keV and increases logarithmically at lower energies. Time-of-flight (ToF) detectors have the potential for the highest energy resolution and lowest background in NDP measurement [32]. However, ToF detector systems used in NDP environment are notoriously difficult to implement and maintain thus they are not in common use. The pixelated detector systems [19] have much potential for 2-, 3-, and 4-dimensional measurement, where the 4^{th} dimension is time. Count rate and energy resolution is not comparable to the other systems but are quite useful for multidimensional applications.

Finally, NDP detection can be performed in coincidence mode [33]. NDP reactions produce two energetic masses of characteristic initial energy and those two particles always are emitted diametrically from the reaction site. For samples that are thin enough that both particles can escape the sample and the sample has parallel faces, the energy-depth resolution is exceptional. This is because of mathematical constraints that can be placed upon the coincident signals [34]. Also, there is no restriction upon the acceptance angle at the detector, so both detectors can be placed as close to the sample as practical and remain out of the neutron beam. The limitation on the sample dimensions and cost limit the applicability of coincidence NDP.

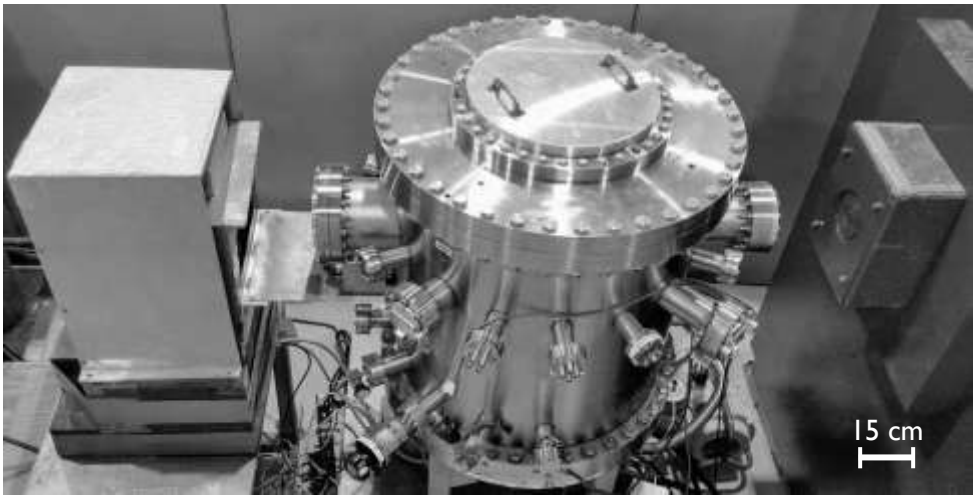

Figure 4. *NDP chamber setup at NG-5 at NIST*. *Left* is neutron beam stop, *center* is the NDP chamber, and *right* is exit of neutron guide.

Conclusion

Neutron depth profiling is a non-destructive, near-surface analyses method which is sensitive to several light elements. Its applications have varied since its conception nearly 50 years ago, with application to the fields of nuclear physics, solid-state chemistry, semiconductor materials, corrosion science, tribology, battery science, and many more. Details of various NDP systems and the compliment of NDP applications can be found through the papers given in reference section.

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References

1. Ziegler, J., G. Cole, and J. Baglin, *Technique for determining concentration profiles of boron impurities in substrates.* Journal of Applied Physics, 1972. **43**(9): p. 3809-3815.
2. Biersack, J., et al., *Range profiles and thermal release of helium implanted into various metals.* Journal of Nuclear Materials, 1979. **85**: p. 1165-1171.
3. Biersack, J., et al., *The use of neutron induced reactions for light element profiling and lattice localization.* Nuclear instruments and Methods, 1978. **149**(1-3): p. 93-97.
4. Downing, R.G. *Historical List of Neutron Depth Profiling Facilities*. 2018 [cited 2018 06/01/2018]; Available from: https://sites.google.com/site/nistndp/earlierfacilitieslist.
5. Biersack, J. and D. Fink, *Implantation of Boron and Lithium in Semiconductors and Metals*, in *Ion Implantation in Semiconductors*. 1975, Springer. p. 211-218.
6. Baum, E.M., et al., *Nuclides and Isotopes: Chart of the Nuclides*. 17 ed. 2010: Knolls Atomic Power Laboratory. 94.
7. Chen-Mayer, H.H., G.P. Lamaze, and S.K. Satija. *Characterization of BPSG films using Neutron Depth Profiling and Neutron/X-ray Reflectometry*. in *AIP Conference Proceedings*. 2001. AIP.
8. Riley, J., et al. *Materials Analysis Using Thermal Neutron Reactions: Applications*. in *Materials Science Forum*. 1984. Trans Tech Publ.
9. Clayton, D.A., J.L. Lacy, and R.G. Downing, *Quality assurance in neutron detector development by neutron depth profiling.* Transactions of the American Nuclear Society, 2006. **95**: p. 397-398.
10. Lamaze, G.P., et al., *Analysis of lithium transport in electrochromic multilayer films by neutron depth profiling.* Surface and Interface Analysis: An International Journal devoted to the development and application of techniques for the analysis of surfaces, interfaces and thin films, 2000. **29**(9): p. 637-641.
11. Lamaze, G.P., et al., *Cold neutron depth profiling of lithium-ion battery materials.* Journal of power sources, 2003. **119**: p. 680-685.
12. Oudenhoven, J., et al., *In Situ Neutron Depth Profiling: A Powerful Method to Probe Lithium Transport in Micro-Batteries.* Advanced Materials, 2011. **23**(35): p. 4103-4106.
13. Lv, S., et al., *Operando monitoring the lithium spatial distribution of lithium metal anodes.* Nature Communications, 2018. **9**(1): p. 2152.
14. Liu, D.X., et al., *In situ quantification and visualization of lithium transport with neutrons.* Angewandte Chemie International Edition, 2014. **53**(36): p. 9498-9502.
15. Nagpure, S.C., et al., *Neutron depth profiling technique for studying aging in Li-ion batteries.* Electrochimica Acta, 2011. **56**(13): p. 4735-4743.
16. Liu, D.X., L.R. Cao, and A.C. Co, *Demonstrating the Feasibility of Al as Anode Current Collector in Li-Ion Batteries via In Situ Neutron Depth Profiling.* Chemistry of Materials, 2016. **28**(2): p. 556-563.
17. Han, X., et al., *Negating interfacial impedance in garnet-based solid-state Li metal batteries.* Nature materials, 2017. **16**(5): p. 572.
18. He, Y., R.G. Downing, and H. Wang, *3D mapping of lithium in battery electrodes using neutron activation.* Journal of Power Sources, 2015. **287**: p. 226-230.
19. Tomandl, I., et al., *High resolution imaging of 2D distribution of lithium in thin samples measured with multipixel detectors in sandwich geometry.* Review of Scientific Instruments, 2017. **88**(2): p. 023706.

20. McWhinney, H.G., et al., *Diffusion of lithium-6 isotopes in lithium aluminate ceramics using neutron depth profiling.* Journal of nuclear materials, 1993. **203**(1): p. 43-49.
21. Trivelpiece, C.L., et al., *Glass Surface Layer Density by Neutron Depth Profiling.* International Journal of Applied Glass Science, 2012. **3**(2): p. 137-143.
22. Uenleu, K., *Helium-3 in nickel-base amorphous metals: Surface features, subsurface microstructure, migration, and release upon annealing*. 1989, Michigan Univ., Ann Arbor, MI (USA).
23. Shimada, M. and B. Merrill, *Tritium decay helium-3 effects in tungsten.* Nuclear Materials and Energy, 2017. **12**: p. 699-702.
24. Gilliam, S.B., et al., *Retention and surface blistering of helium irradiated tungsten as a first wall material.* Journal of Nuclear Materials, 2005. **347**(3): p. 289-297.
25. Neeft, E.A.C., et al., *Helium irradiation effects in single crystals of MgAl2O4.* Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 2000. **166-167**: p. 238-243.
26. Fink, D., et al., *Nitrogen depth profiling using the 14N (n, p) 4C reaction.* Nuclear Instruments and Methods in Physics Research, 1983. **218**(1-3): p. 171-175.
27. Fink, D., et al., *Nuclear track-based biosensing: an overview.* Radiation Effects and Defects in Solids, 2016. **171**(1-2): p. 173-185.
28. Downing, R., et al., *Neutron depth profiling: overview and description of NIST facilities.* Journal of research of the National Institute of Standards and Technology, 1993. **98**(1): p. 109.
29. Ünlü, K. and B.W. Wehring, *Neutron depth profiling at the University of Texas.* Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 1994. **353**(1-3): p. 402-405.
30. Vacik, J., et al., *Neutron depth profiling facility at Nuclear Physics Institute Rez.* Acta Physica Hungarica, 1994. **75**(1): p. 369-372.
31. Downing, R.G., *NIST Neutron Depth Profiling Facility: 2013, invited.* Transactions-American Nuclear Society, 2013. **109**.
32. Çetiner, S., K. Ünlü, and R. Downing, *Development of time-of-flight neutron depth profiling at Penn State University.* Journal of radioanalytical and nuclear chemistry, 2007. **271**(2): p. 275-281.
33. Parikh, N.R., et al., *Neutron depth profiling by coincidence spectrometry.* Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 1990. **45**(1-4): p. 70-74.
34. Trivelpiece, C.L. and J. Brenizer, *Development of a geometric uncertainty model describing the accuracy of position-sensitive, coincidence neutron detection.* Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 2011. **269**(1): p. 45-52.