Field evaporation and desorption ion sources

Isidro Solano

Follow this and additional works at: http://digitalrepository.unm.edu/phyc_etds

Recommended Citation
Isidro Solano
Candidate

Physics and Astronomy
Department

This thesis is approved, and it is acceptable in quality and form for publication:

Approved by the Thesis Committee:

Paul Schwoebel, Chairperson

Wolfgang Rudolph

David H. Dunlap
FIELD EVAPORATION AND DESORPTION ION SOURCES

by

ISIDRO SOLANO

B.S., UNIVERSITY OF NEW MEXICO, 2005

THESIS

Submitted in Partial Fulfillment of the Requirements for the Degree of

Master of Science
Physics

The University of New Mexico
Albuquerque, New Mexico

December 2011
Field Evaporation and Desorption Ion Sources

by

Isidro Solano

B.S., Physics, University of New Mexico, 2006
M.S., Physics, University of New Mexico, 2011

ABSTRACT

Novel approaches to the production of deuterium ions were investigated as part of a program directed toward the development of high efficiency ion source for use in a fieldable neutron generator. The principle line of investigation was a source based on the field desorption of deuterium from the tip surfaces of microfabricated arrays. Using tip arrays, both desorption of atomic deuterium ions and gas phase field ionization of molecular deuterium was observed at fields of roughly 2 V/Å and 2-3 V/Å, respectively, at room temperature. Maximum fields of 3 V/Å have been applied to the array tip surfaces to date, although achieving fields of 2 V/Å to 2.5 V/Å was more typical.
A second line of investigation was proof-of-principle experiments
demonstrating an electrostatic field evaporation based deuterium ion source.
This source produces atomic deuterium and metal ions by the field evaporation
of deuterated metal films. During these studies the morphological structure of
clean and deuterated Er and Ti films deposited on W substrates and their
removal by field evaporation were investigated. It was observed that both
titanium and deuterated titanium films deposited on W substrates at 77 K or 295
K were pseudomorphic with the underlying W <110> substrate. Well-annealed Er
films thicker than ~ 20 layers formed a hexagonal close-packed <0001>
orientated over layer with the Pitsch-Schrader orientation on the W <110>
substrate. The pseudomorphic and hexagonal close-packed character of the
films is retained up to the last atomic layer that forms the film-substrate interface.
Deuterated Er films appear polycrystalline. At 77 K in Ar, annealed Er films field
evaporate at 2.5 V/Å primarily as Er$^{2+}$ and deuterated Er films evaporate at ~ 2.4
V/Å primarily as D$^{+}$ and ErD$_x$$^{2+}$, $0 \leq x \leq 3$. Field evaporation of both clean and
deuterated Er and Ti films showed signs of space charge induced field lowering
when film thicknesses exceeding ~10 layers were field evaporated using 20 ns
duration voltage pulses.

To aide in these investigations a simple tin oxide film deposition technique
using a radio frequency induction heater to allow in situ visualization of the
deposition process and resulting film was developed. Uniform films having
resistivities as low as 2 mΩ-cm with transmittances of approximately 85% in the
visible light spectrum were readily deposited.
# Table of Contents

Chapter 1 ............................................................................................................. 1
  Introduction ....................................................................................................... 1
Chapter 2 .............................................................................................................. 4
  Field Desorption Ion Source Development for Neutron Generators .......... 4
    INTRODUCTION ............................................................................................. 4
    EXPERIMENTAL ............................................................................................ 8
    RESULTS ........................................................................................................ 10
    CONCLUSION ................................................................................................. 19
Chapter 3 ............................................................................................................ 21
  The Growth and Field Evaporation of Er and Deuterated Er Films .......... 21
    INTRODUCTION ............................................................................................. 21
    EXPERIMENTAL ............................................................................................ 22
    RESULTS ........................................................................................................ 25
      Er Film Morphology .................................................................................... 25
      Er-W Interface Morphology ......................................................................... 29
      Deuterated Er Film Morphology ................................................................ 33
    SUMMARY ...................................................................................................... 42
Chapter 4 ............................................................................................................ 45
  A Field Evaporation Deuterium Ion Source for Neutron Generators ..... 45
    INTRODUCTION ............................................................................................. 45
    EXPERIMENT .......................................................... ................................ 47
    RESULTS AND DISCUSSION ................................................................. 49
    CONCLUSION ................................................................................................. 57
Chapter 5 ............................................................................................................ 58
  Deposition of Transparent, Conductive Tin Oxide Films on Glass Using a Radio-Frequency Induction Heater ........................................ 58
    INTRODUCTION ............................................................................................. 58
    EXPERIMENTAL ARRANGEMENT ......................................................... 60
    PROCEDURE AND RESULTS ................................................................. 62
Chapter 6 ............................................................................................................ 67
  Conclusion ......................................................................................................... 67
Chapter 1

Introduction

The prevention of nuclear terror was recently listed by the National Academy of Engineering as one of its fourteen grand challenges for engineering in the 21st century. As they state, “Nuclear reactors for research or power are scattered about the globe, capable of producing the raw material for nuclear devices. And the instructions for building explosive devices from such materials have been widely published, suggesting that access to the ingredients would make a bomb a realistic possibility.” [1] Of the methods prescribed for the prevention of a nuclear terror attack detection of special nuclear material (SNM), such as highly enriched uranium (HEU) and plutonium, plays a central role. The National Academy of Sciences has recommended research and development in the near term into active neutron interrogation sources (neutron generators) and detector systems [2] because of its reliability in the detection of HEU.

Our primary focus has been toward the development of a high yield, man-portable energy efficient neutron generator – something that does not exist
today. Since the target technology for deuterium-tritium neutron generators is well understood the most significant improvement can be achieved by improving the deuterium ion source through increased output and operating efficiency.

Our goal is to incorporate the principles of electrostatic field desorption and electrostatic field evaporation to maximize ion production efficiencies. As such we investigated the optimal conditions for the desorption of deuterium from tungsten and molybdenum surfaces, and determined optimal growth and removal conditions of metal hydride films from tungsten substrates.

I will be presenting a catalog of the publications produced during these investigations starting with the first studies done on field desorption tip array ion sources. This will be followed by the morphological studies of two hydrogen occluders, Ti and Er, and the proof of principle experiments conducted to evaluate their use as a field evaporation driven ion source. The thesis concludes with a short technical paper describing a simple, novel technique for the production of transparent conductive films on glass for use in atom probes and other laboratory devices. A list of these publications follows:


Chapter 1. Introduction

I. Solano and P.R. Schwoebel, “The Growth and Field Evaporation of Clean and Deuterated Erbium Films”, Surface Science (Accepted for publication).
Chapter 2

Field Desorption Ion Source Development for Neutron Generators

INTRODUCTION

Several National and Homeland Security activities involve the detection and identification of special nuclear material (SNM) including highly enriched uranium and plutonium. While passive detection systems can be used in some cases, for the most challenging problems involving shielded SNM it is generally accepted that these materials can only be reliably detected using active interrogation techniques such as neutron interrogation. However, before large-scale neutron interrogation systems can be reliably deployed for this purpose improvements are needed to enhance the performance attributes of the neutron generator and detector technologies; in particular, the National Academy of Sciences has concluded that significant advances in neutron generator technology are required [2].
Chapter 2. Field Desorption Ion Source Development for Neutron Generators

Existing compact, sealed-tube neutron generators create and then accelerate deuterium ($D$) and/or tritium ($T$) ions into $D$ and/or $T$–hydrided metal targets to produce neutrons by the $D$-$D$ or $D$-$T$ nuclear fusion reactions $D + D \rightarrow n + {^3}He$ and $D + T \rightarrow n + {^4}He$. With few exceptions the ion sources in these generators extract ions from a plasma created in various types of electrical discharges [3,4,5]. This leads to generators with either long lifetimes (1000 h) and low outputs ($\sim 10^8$ n/s), such as well logging generators, or high outputs ($> 10^{12}$ n/s) and short lifetimes (a few hours). Both high output, long-lived systems [4,5] and low output man portable systems [6] are under development. For field detection applications one would like to have long-lived, high output generators. Additional desirable generator features include variable pulsing ability, rugged design, low cost, ambient cooling and, in the case of man portable systems, high energy efficiency.

To improve the performance of existing neutron generators we are developing a novel approach for the ion source [7,8]. This ion source uses the electrostatic field desorption (EFD) [9] of deuterium and/or tritium from the surface of metal tips to create atomic ions. The yield of a neutron generator scales with the ion beam current which in turn, for the EFD source, scales with the tip surface area and number of tips. Thus, as shown schematically in Fig. 2.1, an array of tips is being used for the EFD source.
Figure 2.1 Schematic diagram of the deuterium-tritium neutron generator using a field desorption deuterium ion source in a deuterium atmosphere. Voltages $V_1$ and $V_2$ control the deuterium ion accelerating voltage and current respectively.

The EFD source operates in a pulsed mode wherein a voltage pulse ($V_2$ in Fig. 2.1) applies an electric field sufficient to remove, as ions, deuterium and/or tritium atoms that have adsorbed on the tip surfaces from the gas phase. The hydrogen isotope gases are subsequently reabsorbed, at a rate dependent upon the background gas pressure, before another pulse is applied.

Potential key benefits of this type of ion source relative to conventional ion sources are: 1) increased electrical efficiency and reduced power requirements relative to neutron yield to enable effective man-portable systems, 2) scalable neutron output (with the dimensions of the desorption array) to meet different application needs, 3) increased generator and target lifetime due to the use of a distributed ion beam, and 4) a reduction in system complexity due to the elimination of plasma based ion sources.
Figure 2.2 The modification performed to standard Spindt-type arrays to increase the operating voltage. (a) Scanning electron micrograph of a $Si_3N_4$ shielded array. (b) Schematic of the Spindt-type array with a shield of $Si_3N_4$ dielectric.

Here are presented the first studies using modified Spindt-type tip arrays for an EFD ion source produced by our co-collaborators at SRI International, see Fig. 2.2. The integral gate electrode of these microfabricated tip array assemblies permits a high tip packing density, and thereby the potential for large ion currents. This electrode also allows for the straightforward modulation of $V_g$ using relatively low voltages (~1 kV) to achieve field desorption.
EXPERIMENTAL

The experimental chamber is an ultrahigh vacuum imaging atom probe [10] achieving a base pressure in the low $10^{-10}$ Torr range following bake-out at ~ 500 K for 12 h. Species desorbed from the tip surfaces are identified using time-of-flight (TOF) mass analysis with typically an ~12 cm drift distance, and detected using a chevron microchannel plate employing a P-47 phosphor screen. Referring to Fig. 2.1, in the atom probe the target is replaced with the chevron detector and $V_1$ is set to zero in order to obtain a field free drift region between the gate (i.e. grid) electrode and the detector. An Amperex XP2262 photomultiplier tube monitors the output of the phosphor screen and the characteristic ~60 ns phosphor decay time is thus visible in the time-of-flight mass spectra. The voltage pulse applied to the tip electrode ($V_2$ in Fig. 2.1) of the tip arrays to initiate ion desorption was (at the pulse generator) a square wave with a duration of either 20 ns or 100 ns with a rise time of ~2 ns into a 50 Ω load. Analysis of the field electron emission characteristics of the arrays when a negative going pulse was applied to the tip electrode showed a rise time of ~ 4 ns due to impedance mismatches involved in transmitting the pulse to the array. For these experiments only hydrogen or deuterium gas loadings were used in the chamber, tritium was not used.
The tip arrays were 50,000-tip Spindt-type field emitter arrays having molybdenum tips with gate-to-base oxide thicknesses of either 0.5 μm or 1.75 μm [11]. The short tip-to-gate hole rim distance (typically <1 μm) means that mass identification can be difficult because the picosecond flight times of the ions in the acceleration gap are much less than the rise-time of the voltage pulse used to initiate desorption. This allows for variation in the final energy of the ions and therefore greater uncertainty in the ion mass-to-charge ratio (m/z). The TOF system could be calibrated for mass-to-charge ratios less than or equal to 4 m/z by filling the system with H₂ and/or D₂ gas and observing the arrival of, for example, the field ionized molecular ion or atomic fragment. Ion species exceeding 4 m/z are estimated from this low mass calibration procedure. Unless noted otherwise, the tip array field–voltage proportionality factor used to estimate ion emission fields was calculated assuming the onset of electron emission from the arrays (~50 nA) for a given voltage occurred at an electric field at the tip apices, F, of 0.25 V/Å. *In vacuo* heating of the arrays was accomplished using a custom alumina insulated filament to which the TO-5 header holding the arrays was attached. Array temperatures were measured using either an iron-constantan thermocouple attached directly to the TO-5 header or a disappearing filament optical pyrometer. Research grade (99.9999%) hydrogen and/or deuterium gas was admitted directly into the atom probe chamber from 1-liter glass flasks. Studies were conducted at room temperature (293 K) and at 77 K. Results from the studies done at 77 K will be presented in a future paper [12].
RESULTS

Ion emission was first attempted using standard Spindt-type field emitter arrays (0.5 μm thick oxides) at $F < 0.7 \ \text{V/Å}$ (i.e. typically voltages of $V_2 < 250 \ \text{V}$). Attempting to reach fields needed for desorption of atomic hydrogen or deuterium ($F > 1 \ \text{V/Å}$) led to electrical breakdown and damage to the array structures. Two array structure modifications were made that increased the fields achievable at the tip surfaces. The first was to increase the thickness of the insulating oxide layer between the gate and base electrodes from 0.5 μm to 1.75 μm. The second was to incorporate an insulating shield of $Si_3N_4$ in order to suppress electron emission from the gate, see Fig. 2.2. This type of array was used for the remainder of the studies reported herein.

![Graph showing common surface contaminants removed by field desorption from as-fabricated arrays. ($V_2 = 410$ volts, $F = 1.7 \ \text{V/Å}$)](image)

Figure 2.3 Common surface contaminants removed by field desorption from as-fabricated arrays. ($V_2 = 410$ volts, $F = 1.7 \ \text{V/Å}$)
Atom probe studies of as-fabricated arrays, i.e. those that had undergone no post fabrication treatment except hydrogen firing and storage in vacuum until use [13], typically showed a wide variety of surface adsorbates. Figure 2.3 is an example of a mass spectrum showing some of the commonly observed species such as, mass-to-charge ratios of 1 ($\text{H}^+$), 12 ($\text{C}^+$), 18 ($\text{H}_2\text{O}^+$), 24 ($\text{C}_2^+$), and 32 ($\text{S}^+$, $\text{O}_2^+$). Other commonly observed species were 16 ($\text{O}^+$) and 28 ($\text{CO}^+$). The presence of compounds containing $\text{H}$, $\text{C}$, $\text{O}$, and $\text{S}$ on metal surfaces exposed to the atmosphere and subjected to only a mild vacuum bakeout (~500 K), are not unexpected [14].

![Figure 2.4](image)

**Figure 2.4.** The removal of $\text{H}_2\text{O}$ by heating. TOF spectra of an as-fabricated array and the array after heating *in situ* to 800°C for 40 min. ($V_2 = 425 \text{ V}$, $F = 1.9 \text{ V/Å}$)

Adsorbate removal by heating in vacuum could yield predictable results, see Fig. 2.4. In this example, the initial desorption spectra, taken following installation in vacuum and system bakeout, showed the presence of $\text{H}_2\text{O}$ (18) and $\text{CO}$ (28).
After heating in vacuum at ~1133 K for 40 min. the level of $H_2O$ has decreased significantly while the level of $CO$ has remained essentially unchanged. This is consistent with the fact that $CO$ is only totally removed from $Mo$ at temperatures above ~1700 K [15,16]. Typically, longer heating times (>10 h) at temperatures of 1100 K are required to clean the tip surface sufficiently to allow for the adsorption of deuterium.

Future work in this area will permit the use of more advanced cleaning processes including higher temperature hydrogen and vacuum firing. These techniques are commonly employed in the manufacture of sealed tube neutron generators.

![Figure 2.5. TOF spectra of surface contaminants on an as-fabricated array in a partial pressure of $10^{-5}$ Torr of deuterium gas. ($V_2 = 235$ V, $F = 1.3$ V/Å)](image)

Figure 2.5 is a spectrum from an as-fabricated array in an atmosphere of $10^{-5}$ Torr $D_2$, at an applied field of 1.6 V/Å where $H$, $H_2O$ and $C$ are observed. The
source of $H$ is as yet unclear. At times spectra containing only $H^+$ are observed from the as-fabricated arrays suggesting desorption of hydrogen adsorbed from the residual gas atmosphere of the vacuum. When observed with the carbon, dissociation of some hydrocarbon species cannot be ruled out. Additional experiments are being conducted to determine the source of hydrogen in various circumstances. Figure 6 shows the TOF spectrum from the same array in $10^{-5}$ Torr of $D_2$ after heating in vacuum for 12 h at ~1050 K. A significant atomic deuterium peak is now observed. Apparently the level of surface contamination present on the tips of the as-fabricated array inhibited the adsorption of deuterium [16]. This is not surprising, as adsorbate replacement processes are governed by sublimation energetics and the binding energy of hydrogen is lower than species such as $H_2O$ and $CO$, for example.

Figure 2.6. Observation of field desorption of deuterium. TOF spectra of the array used in Fig. 5 after heating to 1130 K for 12 hours in vacuum. Initial spectra taken in $10^{-5}$ Torr of deuterium gas, and subsequent spectra taken after evacuation of the deuterium gas to $10^{-9}$ Torr. ($V_2 = 335$ V, $F = 1.9$ V/Å)
To confirm the deuterium peak was due to desorption and not gas phase field ionization of deuterium, the gas was evacuated to $10^{-9}$ Torr and additional spectra accumulated, as shown in Fig. 2.6. Here there is only an initial slight decrease in the height of the atomic deuterium peak, consistent with desorption of deuterium from the tip surfaces. If the majority of the signal was due to gas phase ionization the peak height would decrease dramatically as the result of such a large decrease in deuterium partial pressure.

According to field desorption studies of deuterium from single wire tips [11], the desorption of deuterium should occur at fields on the order of 3 V/Å. In the case of the arrays, desorption is observed at fields of $\sim$2 V/Å. The reduced field required for desorption could be due to the presence of residual surface contamination onto which the deuterium is adsorbed. As we have only heated the arrays to temperatures of $\sim$1100 K and not yet achieved fields sufficient to field evaporate the tip surfaces ($\sim$4 V/Å for molybdenum) the presence of residual surface contamination would not be surprising.
Chapter 2. Field Desorption Ion Source Development for Neutron Generators

Figure 2.7. The accumulation of CO in the high field region of the tip surfaces with time. TOF spectrum of the array used in Figures 2.5 and 2.6 operating in $10^{-5}$ Torr of deuterium gas after being at $10^{-10}$ Torr for 150 hours. ($V_2 = 335$ V, $F = 1.9$ V/Å)

Following the accumulation of the spectra associated with Figs. 2.5 and 2.6, the array was allowed to remain in UHV for approximately 5 days. After this waiting period desorption spectra at ~2 V/Å and $10^{-6}$ Torr $D_2$ were then dominated by the presence of CO, see Fig. 2.7. This is not surprising as CO typically has a significant partial pressure in baked stainless-steel chambers [17], and would accumulate on the surface at the expense of hydrogen (or its isotopes) [16]. Note that these data also confirm that the deuterium signals shown in Figs. 2.5 and 2.6 are due to desorption and not field ionization, as deuterium signals were not observed under similar applied fields and gas pressures.

It is clear that surface contaminants can inhibit the adsorption of deuterium onto the tip surfaces, a phenomenon that is also in agreement with our studies.
on single etched-wire molybdenum tips [11] and such processes generally. Such contaminants can reach the high field region of the tip surfaces either by adsorption from the gas phase or by diffusion from the tip shank to the high field region. In the case of CO adsorption shown in Fig. 2.7, the time required to accumulate the material is consistent with adsorption from the gas phase, here 150 h at $10^{-10}$ Torr. We assume a standard partial pressure of $\sim 10^{-11}$ Torr of CO and an initial sticking probability of $\sim 1$ [18], meaning that $\sim 100$ hrs is required to form a monolayer of CO.

There are cases where surface diffusion is the major cause of contaminants appearing in the high field region. In this process, contaminants are first removed by field desorption. The resulting contaminant concentration gradient drives surface diffusion to repopulate the high field region with contaminants present on the shank region of the tips. Note that contaminants can also be drawn to high field regions by the field gradient (i.e. polarization forces); however, unlike in conventional atom probe experiments this does not appear to be a major factor here because only pulsed fields as opposed to pulsed and d.c. bias fields are used.
Figure 2.8 shows an inverse relationship between the pulse rate and the amount of contaminants desorbed from the tip apices. The spectrum was taken at an operating pressure of 1x10^-9 Torr (consisting of principally $D_2$) and the pulse rate varied from 0.1 to 10 seconds delay between pulses. With monolayer formation rates due to adsorption from the gas phase at a maximum of ~$10^4$ s/monolayer (for $D_2$ with a sticking probability of ~ 0.1 on clean molybdenum) no significant adsorption should occur on time scales of 0.1 to 10 s. Thus it is reasonable that the observed changes in contaminant levels shown in Fig. 2.8

Figure 2.8 Surface diffusion of adsorbates into the high field region of the tip surfaces. TOF spectra show (a) the variation in the quantity of the species observed as a function of delay time between pulses and (b) the spectrum at a delay time of 5 s. ($V_2 = 425$ V, $F = 1.9$ V/Å).
are due to surface diffusion. Similar experiments [12] conducted at 77 K show a decreased contamination rate, also consistent with surface diffusion processes. Note that the trend observed in Fig. 2.8 also rules out the possibility that a significant fraction of the species observed were produced by gas phase ionization. If there was a significant component due to gas phase ionization, the intensity level of the ions observed would not vary with the pulsing rate.

![Graph showing TOF spectrum](image)

**Figure 2.9** The observation of gas phase ionization of deuterium. TOF spectrum of an array in $10^{-5}$ Torr of deuterium gas at $V_2 = 375$ V, $F = 2.1$ V/Å and at $V_2 = 550$ V, $F = 3.1$ V/Å.

Gas phase field ionization has been observed at room temperature at fields exceeding $\sim 2$ V/Å, in partial pressures of deuterium. Figure 2.9 is a TOF spectrum at a field $\sim 2$ V/Å and 3 V/Å in a $D_2$ partial pressure of $10^{-5}$ Torr. As the field is increased the ratio of atomic to molecular deuterium increases due to field dissociation of the parent molecule [19]. If the applied field was not limited by voltage breakdown of the microfabricated structure and could be increased
further, eventually only atomic deuterium would be observed. The fields predicted using the onset of electron emission are seen to be in reasonable agreement with the fields expected for the onset of hydrogen ionization and dissociation.

**CONCLUSION**

Atom probe studies of field emitter arrays have been conducted for the first time. To date, pulsed voltages applied to the microfabricated tip arrays have been typically limited to \(~550\) V (\(~2.5\) V/Å maximum) due to electrical breakdown. It remains unclear as to whether this limit is related to vacuum, surface, or bulk breakdown processes. We are presently fabricating tip structures with roughly 5 \(\mu\)m of insulating oxide in order to increase operating voltages.

The desorption of atomic deuterium at room temperature from modified microfabricated Spindt type arrays has been observed. Atomic deuterium is often accompanied by the desorption of other mass species involving compounds of carbon, oxygen and hydrogen. Absolute measurement of the number of ions desorbed in a single pulse is presently being quantified.

Surface contamination caused by either diffusion along the shank of the tips or adsorption from the gas phase can have a significant impact on the spectra observed. Cleaning procedures such as field desorption and heating in vacuum to temperatures of the order of 1100 K significantly reduce the observed levels of
contamination. Surface cleaning procedures involving thermal annealing, hydrogen plasma treatment and laser ablation are being investigated as a means to enhance the percentage of deuterium ions relative to all others desorbed from the tip. Undoubtedly, field evaporation of the tips themselves will ultimately be useful for cleaning the tip surfaces and enhancing the uniformity of the ion emission from tip to tip in the array. Contaminant species identification could be made more accurate using pulsed laser desorption, as this circumvents the potential problem of having short flight times in the acceleration gap with voltage pulsing [10].
Chapter 3

The Growth and Field Evaporation of *Er* and Deuterated *Er* Films

INTRODUCTION

A field evaporation driven deuterium ion source for neutron generators is being developed [20] [21]. This source creates deuterium ions by the field evaporation of deuterated hydrogen occluders, such as *Ti* and *Er*. As part of this effort the morphological structure of both *Er* and deuterated *Er* films deposited on W field emitter tip substrates and their removal as ions by field evaporation has been investigated for the first time using the atomic resolution imaging and mass spectroscopic capabilities of the imaging atom probe.

There have been a number of studies of the growth of hexagonal close-packed (hcp) metals on body-centered cubic (bcc) metals [22 – 29]. In many cases it is found that for a <110> oriented bcc substrate, the hcp over-layer has a <0001> orientation [23 – 30]. The hcp over-layers typically assume the Pitsch-
Schrader (PS) or the Burgers orientation relation relative to the $<110>$ bcc substrate. In the PS orientation relation the close-packed bcc $\{111\}$ direction and the hcp $\{2110\}$ directions are misaligned by 5.26 degrees. In the Burgers orientation relation these close-packed directions are aligned with one another [31].

The field evaporation fields of $Er$ and deuterated $Er$ films and the ion species produced, to the best of our knowledge, have not been studied to date.

**EXPERIMENTAL**

![Figure 3.1 Schematic of the imaging atom probe.](image_url)
Chapter 3. The Growth and Field Evaporation of Er and Deuterated Er Films

Experiments were carried out in a stainless steel imaging atom probe, shown schematically in Fig. 3.1, operating at a base pressure in the low $10^{-9}$ Torr range following bake-out at ~ 500 K for 12 h. The details of the system have been discussed previously [20][21]. Etched wire $<110>$ oriented W tips with an end radius of ~200 Å were used as the substrate on which clean and deuterated Er films were grown.

The W tip was spot-welded onto a W support loop which, in turn, was attached to a cold-finger that allowed for operation at ~ 77 K when filled with liquid nitrogen. Two 0.002 inch diameter W leads were attached to the loop, one on each side of the tip, to determine the tip temperature by elemental resistance thermometry [32]. All tip heating was done in zero applied electric field. A channel electron multiplier array provided ion image intensification and served as the detector when the system was operated as an imaging atom probe time-of-flight mass spectrometer [33]. Time-of-flight mass analysis of films was conducted by pulsed field evaporation at 77 K. Pulsed evaporation was done by applying to the tip a pulse evaporation voltage, $V_{\text{pulse}}$, to a d.c. hold voltage, $V_{\text{dc}}$. The compromise between image acquisition and mass analysis in the imaging atom probe at a drift distance of 7 cm means that the mass resolution was not sufficient to resolve molecular ions comprised of $\text{ErD}_x$ for $x = 0$ thru 3 for the single, double, or triple charged species.

High purity Er (99.9%) was thermally evaporated on to a 0.008 inch diameter W coil which then served as a thermal evaporation source for deposition of Er
onto the $W$ tip. The $W$ tip substrate was thermally cleaned by flashing to $\sim 3100$ K and field evaporation prior to the deposition of erbium. During $Er$ deposition, the $Er$ coated $W$ coil was positioned $\sim 0.5$ cm in front of tip and heated at a set temperature for a predetermined time to deposit a given film thickness. $Er$ deposition rates varied from $\sim 0.5$ to $\sim 3$ monolayers per second. The deposition time required for a given film thickness at a given coil temperature was calibrated by field evaporation while ion imaging to count the number of atomic layers comprising film.

Films were deuterated in deuterium partial pressures ranging from $5 \times 10^{-5}$ to 1.5 Torr for exposure times ranging from 10 to 120 s. $Er$ films were also heated to temperatures from $\sim 310$ to 850 K in both ultrahigh vacuum (UHV) and in deuterium pressures ranging from $5 \times 10^{-5}$ to $5 \times 10^{-3}$ Torr for times ranging from 30 to $\sim 90$ s.

Field ion microscopy was conducted at 77 K in one of four gasses depending on the best imaging field required: 4.4 V/Å for $He$, 3.5 V/Å for $Ne$, 2.2 V/Å for $Ar$ and Deuterium [34]. Evaporation fields for $Er$ and deuterated $Er$ films were calculated from these best imaging fields combined with the evaporation field of $W$ at 77 K (5.5 V/Å in $He$) [35]. Field evaporation of the $Er$ film bulk was conducted at 77 K in $Ar$. Field evaporation of the $Er$ film-substrate interfacial layer was conducted at 77 K in $Ne$ unless noted otherwise. Gases were research grade ($99.9999\%$) and admitted to the system from 1-liter glass flasks.
RESULTS

Er Film Morphology

Er films deposited onto the substrate at 77 K did not have a clear single-crystal structure for thicknesses up to 150 monolayers, see Fig.3.2, consistent with previous studies of non-annealed Er films [29]. Common to the films was a low-index plane overlaying the W (110) plane. This is presumed to be a \{0001\}-type hcp plane for reasons that will be more apparent following the discussion of annealed films below. During the field evaporation of non-annealed films several small crystal planes were removed simultaneously at various positions across the surface of the film. The number of layers deposited onto the W tip were determined by counting the number of layers removed from the low index Er plane overlaying the axial W (110) plane. The evaporation field of these Er films was ~ 2.4 V/Å. Evaporation most often occurred smoothly down to the W substrate, however, with films thicker than ~ 100 layers large fractions of the film could evaporate suddenly.
For Er films having thicknesses exceeding ~20 layers, heating of the substrate to temperatures above ~730 K following deposition at 77 K resulted in the formation of single crystal <0001> oriented hcp Er films as shown in Fig. 3.3. A similar structure is seen when Er is deposited onto heated substrates maintained above ~650 K. The temperatures where crystallization is observed is consistent with other studies done on rare earths with similar melting points, including Er [23 – 30].
Figure 3.3 (a) The tungsten substrate prior to deposition of erbium. [He image, V = 5400 V] (b) The annealed (800 K) 45-layer thick erbium film deposited onto the tungsten substrate shown in (a) [Ar image, V = 2650 V].

The growth of the film in Fig. 3.3 is consistent with the PS orientation relation. Such growth has been reported for yttrium and gadolinium films on bcc niobium [25]. Figure 3.4 is a stereographic projection of a <0001> hcp crystal overlaid on the projection of a <110> bcc crystal showing the PS orientation relation between the two crystal types.
Figure 3.4 Stereographic projection of <0001> oriented hcp crystal overlaid on a bcc <110> crystal. Filled and unfilled circles show, respectively, the major and minor planes of the bcc and hcp crystal.

For annealed Er films having thicknesses on the order of 20 monolayers or less, a more pseudomorphic character was observed. As seen in Fig. 3.5 a 12-layer thick Er film (Fig. 3.5b) has a pseudomorphic-like structure whereas a 52-layer thick film (Fig. 3.5c) deposited on the same W substrate under the same conditions has a distinct hcp structure. With thicker films, such as the film shown in Fig. 3.5c, one sometimes observes that the (0001) plane appears to be shifted spatially relative to the (110) plane of the substrate. We believe this is merely
geometrical effect as the result of the deposition being slightly non normal to the tip axis [30].

All annealed \( \text{Er} \) films field evaporated in a smooth and continuous manner allowing for an accurate determination of film thickness. The evaporation field of annealed \( \text{Er} \) films was \( \sim 2.5 \) V/Å.

Figure 3.5 (a) The underlying tungsten substrate prior to deposition of the \( \text{Er} \) film. [\( \text{He} \) image, \( V = 5836 \) V] (b) A 12-layer \( \text{Er} \) film formed by annealing at 816 K following deposition onto the substrate shown in (a) [\( \text{Ar} \) image, \( V = 2777V \)]. (c) A 52-layer \( \text{Er} \) film formed by annealing at 782 K following deposition onto the substrate shown in (a) [\( \text{Ar} \) image, \( V = \sim 3400V \)].

\textit{Er-W Interface Morphology}

Annealed and non-annealed films maintained their crystalline structures up to the \( \text{Er-W} \) interface yet, in both cases, the interfacial layer itself appeared to be highly pseudomorphic with the \( W \) substrate. An example of the interfacial structure for a non-annealed film is shown in Fig. 3.6. Figure 3.6a shows the \( W \) substrate and Fig. 3.6b the non-annealed 14-layer-thick \( \text{Er} \) film following deposition at 77 K. The last complete layer of the film (after field evaporation of
the layers above) is shown in Fig. 3.6c and clearly shows the pseudomorphic character of the interfacial layer. The gradual evaporation of the last layer of the Er film reveals the underlying W substrate. Figure 3.6d is an image showing the surface after partial removal of the last Er monolayer, exposing the W substrate around the 7 o’clock position of the image. Figures 3.6d through 3.6f show that the interfacial layer preserves the structure of the W (110) plane and W <211> planes, as well as the W (111) plane (near the 1 o’clock position). With non-annealed films, the evaporation field of the interfacial layer was ~2.9 V/Å in Ar.
Figure 3.6. Evaporation sequence of the interfacial layer of a non-annealed $Er$ film. (a) The underlying tungsten substrate prior to deposition [He image, $V = 5844$ V]. (b) The 14-layer thick erbium film [Ar image, $V = 2887$ V]. (c) The essentially intact interfacial layer [Ne image, $V = 3476$ V]. (d) Removal of the interfacial over $W<110>$ and its environs [Ne image, $V = 3269$ V]. (e) Further removal of the interfacial to the $\{211\}$ planes [Ne image, $V = 3462$ V]. (f) Removal of the interfacial to beyond the $\{211\}$ planes and approaching the $\{111\}$ plane [Ne image, $V = 3462$ V].

An example of the interfacial structure of an annealed film is shown in Fig 3.7. Figure 3.7a and 3.7b show, respectively, the $W$ substrate and 30-layer thick $Er$ film following deposition at 77 K and annealing at 490 K. The sequence of images in Figs. 3.7c – 3.7f shows the last layer of the $Er$ film as it is gradually field evaporated from $W$ substrate starting at the 7 o’clock position and being removed toward the 1 o’clock position.
Figure 3.7. Evaporation sequence of the interfacial layer of an annealed $Er$ film. (a) The underlying tungsten substrate prior to deposition [$He$ image, $V = 4495 \, \text{V}$]. (b) The 30-layer thick erbium film following annealing at 490 K [$Ar$ image, $V = 2308 \, \text{V}$]. (c) The last layer of $Er$ above the interfacial with interfacial layer hidden by gas phase ionization at the 7 o’clock position [$Ar$ image, $V = 2359 \, \text{V}$]. (d) Removal of the interfacial over $W$ (110) and its environs [$Ar$ and $Ne$ image, $V = 2606 \, \text{V}$]. (e) Further removal of the interfacial to the $\{211\}$ planes [$Ar$ and $Ne$ image, $V = 2814 \, \text{V}$]. (f) Removal of the interfacial to beyond the $\{211\}$ planes and the (110) plane [$Ar$ and $Ne$ image, $V = 2814 \, \text{V}$]. (g) Tungsten substrate after complete removal of interfacial layer [$He$ image, $V = 4580 \, \text{V}$].

The annealed films also maintain their structure up to the interfacial layer. As can be seen in Fig. 3.7c the final layer of the $Er$ above the interfacial layer still maintains an hcp like structure. The interfacial layer for annealed $Er$ also evaporates generally from one side of the $W$ substrate, as can be seen in Figs.
3.7c – 3.7f, and is also the most well-bound layer of Er encountered, requiring a field of evaporation of 3.4 V/Å in Ne, significantly higher than the non-annealed interfacial layer which evaporated at ~ 2.9 V/Å. Following evaporation of annealed films the W substrate in a much more disordered state as can be seen by comparing Figures 3.6f and 3.7f. It is not surprising that some apparent interfacial mixing occurs as the result of annealing.

Notably, when evaporated in deuterium, no significant increase in the evaporation field was required to remove the interfacial layer of either the annealed or non-annealed films. Hydrogen promoted desorption, a well known phenomenon [35], likely explains this observation. Interestingly, the reduction in evaporation field from ~ 2.9 and 3.4 V/Å to ~ 1.8 V/Å, equivalent to a change of ~ 40%, is much larger than the ~20% typically observed as the result of hydrogen promoted evaporation[36]. This large change in field relative to prior observations may be due to lack of studies of metals that form relatively stable hydrides.

**Deuterated Er Film Morphology**

Deuterated Er films tended to assume a structures somewhere between pseudomorphic and polycrystalline. However, in all cases, as with non-deuterated Er films, a large low-index plane was parallel to the axial W (110) plane of the substrate.
Figure 3.8 An hcp Er film subsequently annealed in a deuterium atmosphere. (a) The underlying tungsten substrate prior to deposition [He image, V = 7124 V]. (b) The 54-layer thick erbium film deposited onto the heated W substrate in (a) maintained at a temperature of 655 K [Ar image, V = 3450 V]. (c) Film after being annealed in deuterium atmosphere to at temperature of 655 K (Deuterium image, V = 2987 V]. (d) Film re-imaged in Ar. [V = 3834V].

The W substrate and a 54-layer thick film with an hcp structure deposited at ~1 layer/s with the substrate held at 655 K are shown in Figures 8a and 8b, respectively. Figure 8c is a deuterium ion image of the film shown in 8b after annealing it to 655 K in a deuterium atmosphere at a partial pressure of 5.5 x10^{-5} Torr for ~ 8.5 minutes. It is well known that the uptake of hydrogen by Er is greatly enhanced at elevated temperatures [37-44]. Figure 8d is the subsequent Ar image of the film. Less the low index plane overlaying the W substrate (110)
plane, it was typically difficult to determine a clear crystalline structure for the deuterated films. At times, as in Fig. 8d, the film reflects the symmetry of the bcc substrate but we were unable to discern the fcc or expanded hcp lattice structures seen for, respectively, the dihydride and trihydride [37-31][45][46]. The results obtained were similar whether or not the Er films were annealed prior to exposure to deuterium. The evaporation field of deuterated Er films at 77 K was ~ 1.8 V/Å in a D atmosphere and ~ 2.5 V/Å in an Ar atmosphere. Again, the low evaporation field in the presence of deuterium, is likely related to the well-known effect of hydrogen promoted field evaporation as discussed above.

**Pulsed field evaporation of Er and deuterated Er films.**

*Er submonolayer and multilayer films.*

Figure 3.9 TOF mass spectrum of a submonolayer quantity of Er film \(V_{dc} = 4696 \text{ V}, \ V_{pulse} = 1000 \text{ V}\).
The field evaporation of submonolayer quantities of annealed and non-annealed Er films principally produced charge species of $\text{Er}^{2+}$ and $\text{Er}^{3+}$, with $\text{Er}^{2+}$ dominating the spectrum, see Fig. 3.9. Due to the use of stainless-steel vacuum chamber, all traces of hydrogen in the films were difficult to eliminate.

![TOF mass spectrum of multilayer Er films field evaporated in a single pulse with thickness as a parameter (\(V_{dc} = 1000\) V, \(V_{pulse} \sim 2100\) V for all four films).][1]

Figure 3.10 shows a sequence in which film thicknesses ranging from 8 to 30 layers were field evaporated in a single pulse from the same tip using the same applied voltage. The field evaporation of multilayer Er films again yielded principally $\text{Er}^{2+}$ for film thicknesses up to 32 layers, the thickest removed in a single pulse. Thicker layers tended to be removed catastrophically, destroying the substrate tip.

![TOF mass spectrum of multilayer Er films field evaporated in a single pulse with thickness as a parameter (\(V_{dc} = 1000\) V, \(V_{pulse} \sim 2100\) V for all four films).][1]
As the evaporated film thickness is increased, the ratio of $Er^{2+}$ to $Er^{2+}$ decreases. During our earlier studies of the field evaporation of multi-layer titanium films the decrease in the ratio of higher charge state species to lower charge state species is due space charge lowering of the applied electric field [21]. Note that as the spectra remain dominated by doubly charged as opposed to singly charged species, it is reasonable to assume the $Er$ film is removed as all ions.

It is also clear from Fig. 3.10 that the quantity of $Er$ detected is not proportional to the number of layers evaporated, despite the fact that we are working in a linear region of response for the detector system [47]. At this point we are unsure of the cause of this sub linear behavior. One possibility is that space charge leads to spreading of the beam near the tip and thus the interception of a smaller fraction of the beam by the detector, an effect that increases with current density (i.e. the number of layers evaporated in a given time) [48]. One clear consequence of space charge is the lowering of the field during evaporation of films from the substrate [49][50]. An estimate of the field reduction can be made using a concentric sphere model for the electrode geometry [50],

$$\frac{E_o}{F_o} = (1 - \gamma)$$

with
where \( E_0 \) is the electric field acting at the surface of the ion-emitting anode, \( F_0 \) is the field acting at the same surface in the absence of space charge, \( j_o \) is the current density at the anode surface, \( m / e \) the mass-to-charge ratio of the ions, and \( \varepsilon_o \) the permittivity of free space. \( R \) and \( r_o \) are the radii of the outer and inner spherical electrodes respectively. We take \( R \) as the distance between the tip and the shield aperture, and \( r_o \) as the radius of the tip \cite{50}. For a 1 monolayer film removed in a maximum time of 20 ns, the current density is \( \sim 10^4 \) A/cm\(^2\) and at a minimum time of \( \sim 2 \) ns, the current density is \( \sim 10^5 \) A/cm\(^2\). Using an aperture to tip distance of \( R = 5 \times 10^{-4} \) m and a tip radius of \( r_o = 170 \) Å (the radius of the tip used for the data in Fig. 3.12) and \( F_0 = 3.1 \) V/Å, table 1 shows that the field drops can be substantial.

<table>
<thead>
<tr>
<th>( r_o (nm) )</th>
<th>Layers</th>
<th>( t_{evaporation} (ns) )</th>
<th>Ion</th>
<th>( \gamma )</th>
<th>( E_o / F_o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>5</td>
<td>5</td>
<td>( Er^{++} )</td>
<td>0.065</td>
<td>0.935</td>
</tr>
<tr>
<td>17</td>
<td>10</td>
<td>5</td>
<td>( Er^{++} )</td>
<td>0.150</td>
<td>0.850</td>
</tr>
<tr>
<td>17</td>
<td>15</td>
<td>5</td>
<td>( Er^{++} )</td>
<td>0.302</td>
<td>0.698</td>
</tr>
<tr>
<td>17</td>
<td>5</td>
<td>2</td>
<td>( Er^{++} )</td>
<td>0.208</td>
<td>0.792</td>
</tr>
<tr>
<td>17</td>
<td>15</td>
<td>5</td>
<td>( D^+ )</td>
<td>0.014</td>
<td>0.986</td>
</tr>
</tbody>
</table>

Table 3.1 Approximated reduction in field due to space charge effect.
Deuterated Er submonolayer and multilayer films.

Figure 3.11. Submonolayer quantity of deuterated erbium film field evaporated in ultra-high vacuum.

Independent of the film deuterization procedure used, the evaporation of submonolayer quantities of deuterated Er films was dominated by $D^+$ and $ErD_x^{2+}$ for $0 \leq x \leq 3$. The next most abundant species was $ErD_x^{3+}$. Figure 3.11 is a spectrum resulting from the average of 20 sub-monolayer evaporation pulses with the film in vacuum at 77 K following annealing at 723 K in a deuterium atmosphere of $1.5 \times 10^6$ Torr for ~10 sec.
Figure 3.12. Submonolayer quantity of erbium first evaporated in $10^{-9}$ Torr and then in $10^{-6}$ Torr of deuterium.

When deuterated films were pulse evaporated in a deuterium atmosphere of $\sim 10^{-6}$ Torr, a significant $\text{ErD}_x^{4+}$ appeared. The spectrum in Fig. 3.12 shows the typical $\text{ErD}_x^{2+}$ and $\text{ErD}_x^{3+}$ ratio for a film evaporated in $10^{-9}$ Torr. With the addition of $\sim 10^{-6}$ Torr deuterium an $\text{ErD}_x^{4+}$ peak now appears and there is a substantial increase in the quantity of material removed at the same voltage (field). The increased amount of material is expected due to the lower fields necessary for the removal of the film in a hydrogen atmosphere (1.8 V/Å) due to promoted evaporation, mentioned previously. The presence of $\text{ErD}_x^{4+}$ may be the result of a field adsorbed deuterium layer on the surface leading to the formation of additional Er-deuterium compounds. Similar field adsorption effects are known to lead to the formation of metal-inert gas ion complexes during field evaporation [15].
Chapter 3. The Growth and Field Evaporation of Er and Deuterated Er Films

Multilayer deuterated Er films were also removed in a single 20 ns duration pulse. Figure 3.13 shows a series of spectra taken with film thickness as a parameter. As with Er films, the total ion yield is again not proportional to the film thickness. Also, as with Er films the doubly charged ErD$_x^{2+}$ species dominates the mass spectra. The spectra also show a decrease in the ratio of ErD$_x^{3+}$ to ErD$_x^{2+}$ and the appearance of ErD$_x^+$ with increasing film thickness, again due to space charge lowering the applied field at the tip.

Ratios of D$^+$ to ErD$_x^{2+}$ typically remained ~1 for film thicknesses ranging from 2 to ~15 layers as can be seen in Fig. 3.12. For thicker films, the ratio gradually decreased to ~0.5:1 by ~50 layers, the thickest removed in a single pulse. Higher ratios were expected given the propensity for Er to form di- and tri-hydrides [38-46] but as with our earlier studies of deuterated Ti [21], these observations are again consistent with space charge lowering of the applied field. A decrease in applied electric field leads to less dissociation of Er-deuterium molecular complexes and thus a decrease in the quantity of atomic (or molecular) deuterium ions produced during pulsed evaporation as the number of layers is increased.
Figure 3.13. Field evaporation of multilayer deuterated erbium films in a single pulse with film thickness as a parameter.

**SUMMARY**

During the field evaporation of non-annealed films several small crystal planes were removed simultaneously at various positions across the surface of the film. The evaporation field of these Er films was ~ 2.4 V/Å in Ar. Evaporation most often occurred smoothly down to the W substrate, however, with films thicker than ~ 100 layers large fractions of the film could evaporate suddenly. All annealed Er films field evaporated in a smooth and continuous manner allowing for an accurate determination of film thickness. The evaporation field of annealed Er films was ~ 2.5 V/Å and proceeded smoothly through the film down to the
interfacial layer. Evaporation of interfacial layers also occurred smoothly across the face of the substrate but at fields much larger than those of the bulk material above it. With non-annealed films, the evaporation field of the interfacial layer was ~2.9 V/Å in Ar. The interfacial layer for annealed Er was the most well-bound layer of Er encountered, requiring a field of evaporation of 3.4 V/Å in Ne. Notably, when evaporated in deuterium, no significant increase in the evaporation field was required to remove the interfacial layer of either the annealed or non-annealed films and allowed for a reduction in evaporation field from ~ 2.9 and 3.4 V/Å to ~ 1.8 V/Å, equivalent to a change of ~ 40%. For the bulk material the evaporation field of deuterated Er films at 77 K was ~ 1.8 V/Å in a D atmosphere and ~ 2.5 V/Å in an Ar atmosphere. The low evaporation field in the presence of deuterium, is likely related to the well-known effect of hydrogen promoted field evaporation as discussed above.

For film thicknesses above ~20 layers, Er grows as a single crystal <0001> oriented film on W (110) for substrate temperatures above ~650 K during deposition or with post deposition heating to ~730 K following deposition at 77 K. At lower temperatures the film structure tends to be polycrystalline but maintains a {0001} Er plane parallel to the {110} W plane. Films less than 20 layers in thickness tend to form a more pseudomorphic structure. In both cases the morphology was maintained up to the Er–W interface. The interfacial layer evaporated at substantially higher fields than that of the bulk film. The deuterated Er films tended to form a structure somewhere between pseudomorphic and
polycrystalline, yet maintained the coincidence of the $Er\{0001\}$ and $W\{110\}$ planes.

Pulsed evaporation in ultra high vacuum of both clean and deuterated $Er$ films principally produced charged species of $Er^{2+}$, $Er^{3+}$, and $ErD_x^{2+}$, $ErD_x^{3+}$, respectively, along with $D^+$ for the deuterated films. When deuterated films were pulsed in a deuterium atmosphere of $> 10^{-6}$ Torr significant peaks of $ErD_x^{4+}$ were observed. Ratios of deuterium to $Er$ typically remained $\sim 1$ for film thicknesses $< 15$ layers but decreased to $\sim 0.5:1$ for 50-layer-thick films due to space charge lowering of the applied fields. The use of pulses with rise-times $> 100$ ns will be investigated as a method for dissociating greater quantities of the $Er-D$ molecular complexes by reducing the effects of space charge.
Chapter 4

A Field Evaporation Deuterium Ion Source for Neutron Generators

INTRODUCTION

A key component of homeland and national security activities is the detection of special nuclear material, and in particular highly enriched uranium (HEU). As noted in a recent report published by the National Academy of Sciences, improved neutron generators are needed for HEU detection [2]. In particular fieldable systems require generators that are compact, reliable, and low cost, yet provide sufficient output to enable practical detection scenarios. Fieldable detection system needs vary from man-portable units to fixed systems for the interrogation of large sea-going shipping containers.

There is also interest in developing so-called 'stand-off' systems capable of detection at distances of many tens of meters to in excess of one kilometer. The mean free path $\lambda$ of gamma-rays and neutrons in the atmosphere ($\sim 100$ m), and
the $1/r^2$ dependence of typical probe beam and return signal intensities for isotropic radiation, limit the standoff distance $r$ due to a signal attenuation factor that varies as $e^{-\lambda/r^4}$. However placing a high output, easily portable, neutron source, or even a highly capable ultra-compact and possibly disposable interrogation system, close to the target circumvents some signal loss.

Existing compact neutron generators are sealed-tube accelerators that drive the deuterium-tritium ($DT$) fusion reaction $^3H(dn)^4He$. This reaction is used because it has a large cross-section at relatively low energies. Key to improving the performance of compact generators is improving operational aspects of the ion source, such as for example increasing the deuterium yield and reliability while decreasing complexity and cost. Ion sources for neutron generators generally employ some form of electrical discharge, ranging from low pressure Penning discharges to arc discharges and plasma focus-types [53]. Ion sources not based on electrical discharges include those using field ionization [6] or field desorption of deuterium [7][8]. These later types provide high energy efficiency in the ion production stage although, contrary to our proposed approach, are more sensitive to surface chemical conditions.

Compact and easily portable neutron generators often function in a pulsed mode and, due to their typically modest output of $\sim 10^5$ neutrons/pulse, operate at frequencies of a few kHz for several seconds or longer in order to provide the neutron fluence required for interrogating targets. In most detection scenarios a single neutron pulse (i.e. $\ll 1$ s in duration), if of sufficient magnitude, could also
be used for interrogation. This approach reduces background and, for a given neutron fluence delivered to the target, results in a net increase in target activity. Simple estimates show that pulses of the order of $10^{10}$ neutrons provide some significant detection capability.

Here we present results demonstrating the feasibility of using the field evaporation of deuterated titanium as an intense pulsed source of atomic deuterium ions for $DT$ neutron generators. Field evaporation is a process by which surface atoms of a solid (or liquid) are removed as ions in an electric field of the order of several V/Å [9].

**EXPERIMENT**

Experiments were conducted with a stainless-steel imaging atom probe [10] operating in the low $10^{-10}$ Torr range. Time-of-flight (TOF) mass analysis of the evaporated ion species produced by the ion source was conducted using a 20 ns duration voltage pulse for field evaporation. The pulse generators used were of the cable discharge type switched by either mercury wetted reed relay (maximum pulse voltage of ~2.5 kV) or a high-pressure spark gap (maximum pulse voltage ~20 kV). A d.c. ‘holding’ voltage could be applied in addition to the pulsed voltage used for evaporation. The field evaporated ions were detected using a chevron channel electron multiplier array whose output was viewed on a P-47 phosphor
screen with an Amperex XP2262B photomultiplier tube. Field evaporation occurred from the apex region of a needle shaped tungsten tip having an end radius, \( R \), of typically 100 Å to 300 Å, measured to an accuracy of \( \sim 10\% \) by correlating the evaporation field \( F \), to the applied voltage, \( V \), through \( F \sim V/5R \) [33]. The small radius of curvature of the tip end form allowed for the application of the high electric fields required for field evaporation of the deuterated films \( (~2.3 \text{ V/Å}) \) using modest voltages (a few kV). Deuterated titanium films were formed in situ by the evaporation of titanium onto the tungsten tip at rates between 0.2 and 2 monolayers per second in \( ~10^{-3} \) Torr of deuterium with a source to substrate distance of \( \sim 1 \) cm. Titanium was evaporated by joule heating of a 0.010 inch diameter coil of Kemet \( Ti-Ta \) alloy wire. Depositions were done at tip substrate temperatures of 77 K and 295 K. Single tungsten needle tips were typically used for up to 100 film deposition and field evaporation sequences. Voltage pulsing conditions were set such that the entire deuterated film was evaporated with a single pulse without removing the tungsten substrate. Evaporation fields were calibrated by helium and hydrogen ion imaging fields \( (~4.5 \text{ V/Å} \) and \( ~2.3 \text{ V/Å} \) respectively) and the tungsten evaporation field \( (~5.5 \text{ V/Å} \) at 77 K) [52].
RESULTS AND DISCUSSION

Ion imaging of both titanium and deuterated titanium films deposited with substrate temperatures of 77 K or 295 K showed the films to be pseudomorphic with the underlying tungsten substrate. Figure 4.1 shows ion images of the initial tungsten substrate and the overlaying deuterated titanium film. The <110> orientation of the tungsten substrate is retained by the deuterated titanium film up to thicknesses exceeding 77 monolayers, the thickest layers imaged to date. The films with the highest pseudomorphic character were achieved with deposition onto a very clean (heated to ~ 1500 K and subsequently field evaporated) tungsten substrate. Interestingly, tungsten is body-centered-cubic (bcc), titanium is hexagonal close-packed up to ~ 1160 K where it transitions to body-centered-cubic, and titanium deuteride has a face-centered-cubic fluorite type structure. The pseudomorphic behavior of titanium on tungsten for coverages up to 4 monolayers has been reported in the past [53], however here this pseudomorphic behavior persists for at least 77 monolayers and occurs with deuterated films.
Figure 4.1. Field-ion microscope images of the tungsten tip with and without a deuterated titanium coating. (a) The tungsten tip imaged in a helium pressure of \(~10^{-5}\) Torr. (b) The deuterated titanium film imaged in a deuterium pressure of \(~10^{-5}\) Torr. The arrow indicates the position of the bcc \(<110>\) crystal plane in both images.

This difference may be due to the more thoroughly cleaned and atomically smooth tip surface provided by thermal heating and field evaporation in the present experiments. In addition the apparent formation of deuterated titanium
thin films with the titanium in a bcc type crystal structure appears to be a new observation. Additional studies of the morphology and equilibrium form \((Ti_xD_y)\) of this deuterated film are underway.

The deuterated titanium layers can be field evaporated layer by layer in a controllable manner in fields of \(~2.3\) V/Å in deuterium background pressures of \(~10^{-5}\) Torr. The evaporation of the deuterated titanium film, due to its pseudomorphic nature, is difficult to distinguish from the field evaporation of the tungsten substrate when ion imaging, with the exception of the dramatic increase in evaporation field required once the tungsten substrate is reached (\(~5.5\) V/Å for tungsten compared to \(~2.3\) V/Å for the deuteride). This controllable evaporation of the film in combination with ion imaging allows us to calibrate the output of the detector to the number of ions removed from the tip surface to an accuracy of \(~20\%\) (\(~10\%\) error in the tip radius and \(~10\%\) error on the number of layers). To calibrate the detector a deuterated film is formed on the surface of the tungsten tip under given deposition conditions. The number of atomic layers comprising the film is then counted by removing the film atomic layer by atomic layer by field evaporation while ion imaging at 77 K in deuterium. A subsequent film is then formed under identical deposition conditions and removed with a single voltage pulse for analysis by TOF mass spectrometry, thus simultaneously yielding a measure of the number of layers removed and identification of the ion species produced.
Figure 4.2. Two time-of-flight mass spectra from the field evaporation ion source show the variation of the deuterium to titanium ion ratio encountered. Atomic deuterium and atomic titanium ions are produced by the field evaporation of a deuterated titanium film. The number of atomic layers of evaporated film is shown.

Figure 4.2 shows TOF mass spectra resulting from the removal of deuterated titanium films by field evaporation. Films with thicknesses ranging from less than 10 to over 120 monolayers have been evaporated to date. The upper limit to the film thickness that can be evaporated in principally atomic form is being investigated. The spectra observed do not vary significantly with film thickness or the temperature at which the film was formed (77 or 295 K), or the temperature of the substrate during field evaporation (77 K or 295 K). Figure 4.3 shows TOF spectra for deuterated titanium films formed and subsequently evaporated at 77 K and 295 K. No statistically significant difference between mass spectra taken at these two temperatures has yet been identified. The TOF mass spectra observed
show only the presence of atomic deuterium ions, $D^+$, molecular ions $D_2^+$ and doubly charged titanium ions, $Ti^{2+}$. At times very small peaks associated with $Ti^{2+}$ or $Ti^+$ are observed. The formation of multiply charged titanium ions is expected [35]. The ratio of the peak heights is representative of the relative number of ions detected. The peak decay time is limited by the decay time of the P-47 phosphor and thus corrections are made to determine the absolute height of peaks such as those corresponding to $D_2^+$ which ride on the tail of the $D^+$ peak. The field evaporation of deuterated films to date has shown $D$ to $Ti$ ratios ranging from ~1 to 2.5, not inconsistent with the presence of $TiD_2$ films in some cases. We are presently correlating the $D$ to $Ti$ ratio observed in the mass spectra with the film deposition and removal conditions. Thus far $D_2^{+}/D^+$ ratios of ~20 to 30% have been observed. The quantity of the $D_2^+$ cannot be accounted for either by gas phase ionization or the evaporation of surface species. The impact of quantities such as the film thickness desorbed and the deuterium content of the film on this ratio is being studied.
Figure 4.3. Time-of-flight mass spectra from the field evaporation ion source for deuterated titanium films formed and evaporated at 77 K (solid line) and formed and evaporated at room temperature (dashed line).

The number of coulombs of deuterium (and titanium) removed from the tip surface can be calculated using the calibration of the thickness of the evaporated film combined with the tip area. With the number of coulombs of deuterium ions produced per tip the number of neutrons produced per tip given the deuterium ion energy and target material can be accurately predicted. For example, with an atomic deuterium ion energy of 120 kV and a thick TiT$_2$ target, the neutron yield is $\sim 10^8$ n/$\mu$C of $D^+$ [54]. Based on this nominal yield Fig. 4.4 is a nomogram showing the number of neutrons produced per tip for a given tip radius and deuterated film having an average of two deuterium ions per titanium ion. The approximate error in the number of neutrons produced is $\sim$20%, i.e. equal to our measured error in the number of evaporated deuterium ions. The white region is
the area explored in the present proof-of-principle studies. Regions highlighted in light and medium gray are those in which no problems are anticipated in accessing. Limits on the tip radius to be \( \sim 0.1 \mu m \) or less are imposed by other issues as discussed below. Highlighted in dark gray is a region wherein the film thickness can significantly exceed the diameter of the substrate tip and it is not clear whether a significant portion of the region is accessible.

![Figure 4.4](image)

**Figure 4.4.** Nomogram showing the number of neutrons that could be produced per tip for a given tip radius and deuterated film thickness. See the text for a discussion of the shaded regions.

It is clear that to achieve the number of neutrons needed in a single pulse for detection applications (\( \sim 10^{10} \) or greater) an array of source tips will be required. Figure 4.5 shows a schematic of a deuterium-tritium neutron generator based on a field evaporation deuterium ion source using an array of tips. The voltage applied between the tips of the array and the target electrode (\( \sim 120 \) kV) accelerates the ions created by the ion source. The ion source consists of the tip
and grid electrodes. The voltage applied between these electrode (~2 kV) produces the field at the apex region to field evaporate the deuterated metal film.

Figure 4.5. Schematic of a neutron generator based on a field evaporation deuterium ion source. The voltage between the evaporation array and the target controls the ion accelerating potential. The voltage between the array the grid electrode controls the deuterium ion current, respectively. Once the magnitude of the voltage between the grid and array is sufficient to result in an electric field of ~2.3 V/Å in the environs of the tip apices, the metal deuteride film present in this region is field evaporated as deuterium and metal ions.

We are presently investigating the use of modified microfabricated field emitter arrays [55] to provide the necessary $D^+$ currents. Tip packing densities are limited to ~$10^7$ tips/cm$^2$ by the microfabrication techniques presently employed. Array areas can easily exceed 10 cm$^2$ as a monolithic structure and 100 cm$^2$ by tiling. Modeling has shown that tip radii of ~0.1 μm will be near the maximum usable with our microfabricated structures due to voltage hold-off limitations [56]. Referring to Fig. 4.4, it can be seen that the neutron yield per cm$^2$ of tip array should comfortably be $10^9$ neutrons per cm$^2$ of array area with $10^{10}$ neutrons per cm$^2$ of array area near the upper bound. In addition we note that the $D^+$ is created in time intervals of ~1 to 10 ns, i.e. less than the time interval of the
applied voltage pulse [10]. Thus the neutrons would be produced in time intervals of 1 to 10 ns and the neutron production rates are very large, of the order of $10^{17}$ to $10^{19}$ neutrons/s. Combining such rates with neutron yields of the order of $10^{10}$ neutrons, the high spatial confinement of the neutron pulse (5 cm with a 1 ns duration pulse) used for interrogation could aid detection applications by, for example, allowing for the use of coincidence techniques to reduce noise.

**CONCLUSION**

The principles underlying a deuterium ion source for deuterium-tritium neutron generators using the field evaporation of deuterated titanium films have been demonstrated. Measurements show that this type of ion source has the potential to provide very high neutron outputs in a single pulse. Note that it is not necessary to evaporate all of the metal deuteride film in a single pulse and that, multiple pulse operation can be implemented for source validation or reduced yield neutron interrogation.
Chapter 5

Deposition of Transparent, Conductive Tin Oxide Films on Glass Using a Radio-Frequency Induction Heater

INTRODUCTION

Tin oxide films are commonly used as a transparent conductive coating on glass substrates. Although in many applications indium tin oxide films have displaced tin oxide films due to their typically lower electrical resistivity [59], tin oxide coatings are often more readily deposited in the research laboratory environment and/or on non-planar surfaces. One common application in the scientific research setting is to apply such a coating as a first step in the preparation of phosphor screens [33][58]. A standard method for the deposition of conducting tin oxide on glass surfaces involves heating the glass substrate in
an oven and exposing it to the vapor formed over molten stannous chloride[33][58]. The drawback to this approach is that because the substrate is located within an oven it is typically difficult to see the substrate during the film deposition process, thereby making it problematic to judge the completeness and uniformity of the coating prior to removal from the oven.

We have implemented a tin oxide deposition procedure that employs a radio frequency (RF) induction heater to heat both the glass substrate and the stannous chloride. This approach allows for the use of glass containers and thus enables clear in situ visibility of the film deposition process and resulting film. The in situ visualization of the substrate during film deposition facilitates the deposition of complete and uniform films.
EXPERIMENTAL ARRANGEMENT

Figure 5.1. Schematic of the apparatus used to deposit tin oxide films. (A) Glass substrate, (B) 3/8 in. thick stainless-steel substrate heater disk, (C) 100 mm Pyrex petri dish, (D) 1000 ml Pyrex beaker, (E) Alumina crucible (R. D. Mathis Part Number C5-AO), (F) 125 ml stainless-steel beaker, (G) Stainless-steel lid with clearance hole in center for ¼ in. copper tube, (H) ¼ in. OD copper tube assembly, (I) 0.030 in. stainless-steel wire cradle for the beaker, (J) Copper coils of induction heater, (K) Lab jack, (L) 600 ml Pyrex beaker, (M) Ventilation hose connected to fume hood.
A schematic of the experimental arrangement is shown in Fig. 5.1. The substrate (A) rests on a 3/8 in. thick stainless-steel substrate heater disk (B) that is slightly larger in diameter than the substrate. The disk in turn rests on a 100 mm diameter petri dish (C) so as to minimize heat transfer to the 1000 ml Pyrex beaker (D). The stannous chloride is held in an alumina crucible (E) which in turn is placed within a 125 ml stainless-steel beaker (F). Eight ¼ in. holes were drilled into the bottom of the beaker to allow for the escape of the vapor formed over the stannous chloride. The stainless-steel beaker is covered with a stainless-steel lid (G) containing a 5/16 in. hole in its center such that a ¼ in. outside-diameter (OD) copper tube (H) could be introduced into the beaker. The stainless-steel beaker is suspended from the top of the 1000 ml Pyrex beaker by 0.030 in. diameter stainless-steel wire (I). The 1000 ml Pyrex beaker resides within the copper coils (J) of the RF induction heater. The RF induction heater is a 5 kW Westinghouse Model 5574 operating at 450 kHz. The copper coils are of a slightly larger diameter than the 1000 ml beaker so that the beaker can easily be raised and lowered with a lab jack (K) in order to heat either the substrate by heating the stainless-steel disk (B), or the stannous chloride by heating the stainless steel beaker (F). The 1000 ml Pyrex beaker rests on an inverted 600 ml Pyrex beaker (L) that in turn rests on the lab jack to insure that the lab jack was well removed from the coils of the generator. Oxygen is introduced directly into both the stainless steel beaker and 1000 ml Pyrex beaker by ¼ in. OD copper tubing (H). The copper tubing enters at the center of the stainless-steel beaker and along the inner diameter of the 1000 ml Pyrex beaker. In the Pyrex beaker
the tube end is bent horizontally to promote better circulation and thus a more uniform flow of the vapor over the substrate. Finally the top of 1000 ml Pyrex beaker is covered by a ventilation hose (M) connected to a fume hood to allow for safe removal of the stannous chloride vapor produced during the deposition.

PROCEDURE AND RESULTS

The temperatures of the substrate and stainless-steel beaker were calibrated as a function of time and RF power level for a given heating coil geometry, i.e. RF coupling. During this calibration the deposition procedure was followed while monitoring both the temperature of substrate with an iron-constantan thermocouple attached to its center by colloidal silver paint and the temperature of the stainless-steel beaker with an iron constantan thermocouple spot-welded to its bottom. Once this calibration was complete the conditions were sufficiently reproducible that monitoring of the temperature during subsequent depositions was not required.
Figure 5.2. Photographs of the tin oxide deposition process. a) The starting position where the glass substrate is brought to ~ 520° C by centering the substrate heater disk (B) in the induction heater coils. The stainless steel beaker (F) is visible within the 1000 ml Pyrex beaker (D) with both residing just above the induction heater coils (J). b) The heating of the stannous chloride. The stainless-steel beaker has been lowered to be centered in the induction heater coils. The hot substrate heater disk (B) is visible just below the induction heater coils. The ventilation hood (M) is seen above the induction heater coils. c) The deposition of the tin oxide. Oxygen is blown simultaneously into the stainless-steel and 1000 ml beakers. Some vapor can be seen above the induction heater coils. Below the level of the coils one can see vapor over the substrate heater disk (B) and substrate (A).

Film deposition proceeded as follows. The lab jack height was adjusted to the starting position where the substrate heater (B) is centered in the coils, Fig. 5.2a.
The induction heater was operated until the glass substrate reached a temperature of ~790 K in 15 minutes. The induction heater power was then reduced by 20% and the lab jack was lowered to the deposition position such that the stainless-steel beaker containing the stannous chloride was centered in the coils and the substrate was below the coils as shown in Fig. 5.2b. Heating in the deposition position continued for 10 minutes at which point the stainless-steel beaker reached a temperature of ~420 °C and the temperature of the substrate had dropped to ~690 K. At this point significant vapor was produced above the stannous chloride, see Fig. 5.2c. Oxygen at a pressure of 3 – 4 psi was then blown simultaneously into the stainless steel beaker containing the stannous chloride and the 1000 ml Pyrex beaker via the copper tubing (H). Three to five bursts of oxygen lasting approximately 3 seconds at 15 second intervals resulted in a visually uniform coating of tin oxide on the substrate. Note that when changing the substrate, the stainless-steel substrate heater disk was sandblasted to prevent flaking of built-up steel oxide onto the new substrate during the subsequent deposition.

These studies examined the deposition of tin oxide onto 2.5 and 3.0 in. diameter Pyrex glass and quartz substrates. In principle a wide variety of substrate sizes and shapes can be accommodated by proper geometrical configuration of the induction heater coils and substrate heater (B). The uniformity of the deposited films was sufficient to produce variations of less than ±5% in resistivity across the substrate. The minimum resistivities achieved were measured with a 4-point probe to be 2.0 mΩ-cm. The resistivity of the tin oxide
Chapter 5. Deposition of Transparent Conductive Tin Oxide Films on Glass

films, could be varied from 2.0 mΩ-cm to greater than 5.0 mΩ-cm by changing the deposition time from ~90 s to ~30 s, respectively. These tin oxide resistivities are comparable to the lowest achieved by others with a variety of approaches including chemical vapor deposition [57][69] and electron beam evaporation [60]. Indium-tin oxide films can have resistivities approaching 0.2 mΩ-cm [57][60][61].

The ratio of the transmittance of coated to uncoated samples for fluorescent room light was typically ~85% as measured with a J6523 Tektronix narrow angle luminance probe. This is similar to measured transmittances of other tin-oxide [57][59] and indium-tin-oxide films [57][62][63].

![Figure 5.3](image)

Figure 5.3. a) Scanning electron micrograph at 120,000 X magnification showing a 27 nm thick tin oxide layer on a quartz substrate. The resistivity of this sample was 735 Ω/square. b) Scanning electron micrograph at 100,000 X magnification showing the grain structure of the tin oxide film in Fig. 3.

Figure 5.3a shows a cross-section of the 27 nm thick film on the quartz substrate. A 4-point probe measurement of this film yielded ~ 735 Ω/square or a resistivity of 2.0 mΩ-cm with a variation of less than ±0.1 mΩ-cm across the
sample. The structure of this film showed grain sizes averaging roughly 25 nm in diameter as shown in Fig. 5.3b. The highly crystalline nature of the films is expected at the high temperature growth conditions used for these depositions [57].

As these measurements demonstrate the produced tin oxide films are both highly uniform and approach the levels of resistivities produced using other more complex methods, such as CVD, and yet can be easily produced in any lab with access to an RF induction heater.
Chapter 6

Conclusion

In our development of high yield man portable neutron generator we have investigated desorption of deuterium from both tungsten and molybdenum surfaces and carried over the principles learned to microfabricated arrays and carried out the first successful desorption of deuterium ions from these arrays. We also conducted studies of two types of hydrogen occluders, titanium and erbium, determining optimal conditions for the hydration of the film and their removal from tungsten substrates. In doing so we were able to demonstrate real-space atomic resolution images showing a Pitsch-Schrader orientation relation between hcp erbium and bcc tungsten and, while removing the occluder films, noted the field lowering effects due space-charge. The information presented in these studies will aide in the future production of a man-portable, high yield neutron generator for the detection of special nuclear materials.
REFERENCES


[38] M. Gasgnier, J. Ghys, G. Schiffmacher, CH. Henry La Blanchetais, P.E. Caro, C. Boulesteix, CH. Loier, B. Pardo, Rare-Earth Hydrides and Rare-Earth Oxides in and from Thin Films of Rare-Earth Metals, J. Less-Common Met. 34 (1974) 131-142.


