Rutherford Forward Scattering and Elastic Recoil Detection (RFSERD) as a Method for Characterizing Ultra-Thin Films*

SAND2013-5128P

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OUTLINE

- Memristors 101
  - Sandia-HP Ta_2O_{5-x} devices
  - Need to measure x accurately
- RBS
  - Works adequately for films > 100nm
  - First results for Sandia films used to calibrate flow rate of O_2 in Magnetron Sputtering System
  - Different IBA technique needed if thinner
- Rutherford Forward Scattering + Elastic Recoil Detection – RFSERD
  - Experiment
  - Theory
  - Advantages vs. Disadvantages
    - Accurate down to a few nm
    - But need to control and reproduce scattering/recoil angle very precisely
    - Most systems will require standards
- Future Work

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Memristors

- Materials that have field dependent resistance have been studied for over 5 decades
- Memristors circuits may replace flash NVMs
- SNL has a Ta_2O_{5-x} memristor based redox memory (ReRAM) cell development project with HP
  - two terminal metal/insulator/metal device
  - resistance modulated by applying a “set/reset” voltage
  - read operation does not change the resistance state
  - Set/reset cycle can be performed many times (up to 10^{12}).
  - May be insensitive to radiation (SNL paper at upcoming NSREC Meeting).
- Measurement and control of the memristive layer stoichiometry is important

The field-induced abrupt resistance switch of memristic materials is not fully understood, but it is clear that control of the composition of the insulating layer in the MIM structure is key

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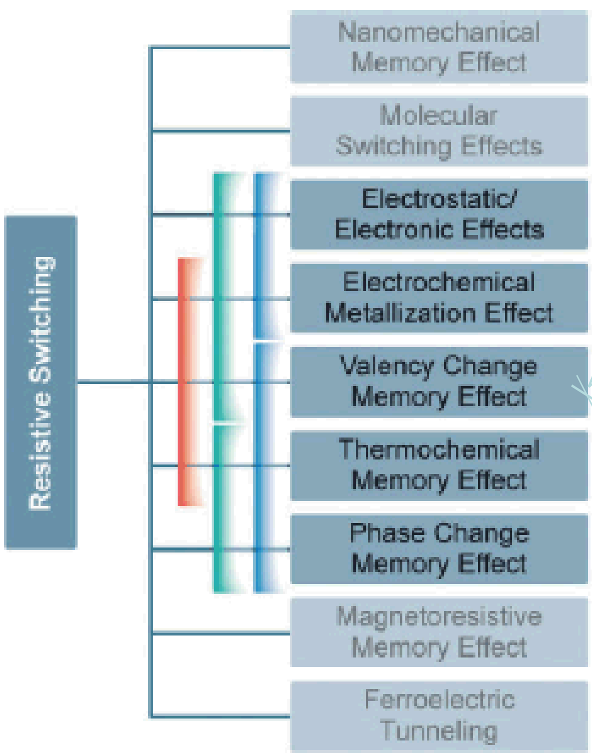
Redox-Based Resistive Switching Memories – Nanoionic Mechanisms, Prospects, and Challenges

By *Rainer Waser,* Regina Dittmann, Georgi Staikov,* and *Kristof Szot*

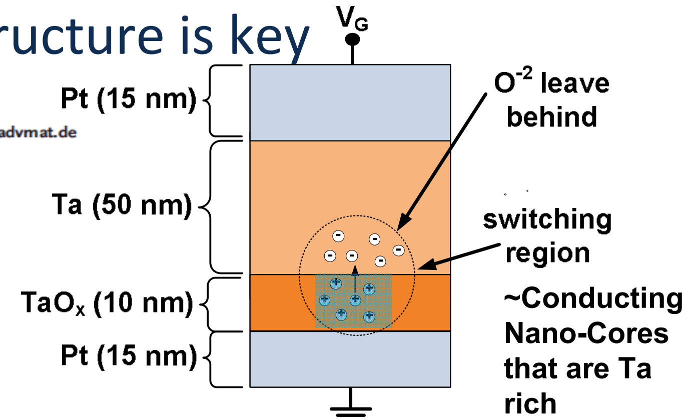


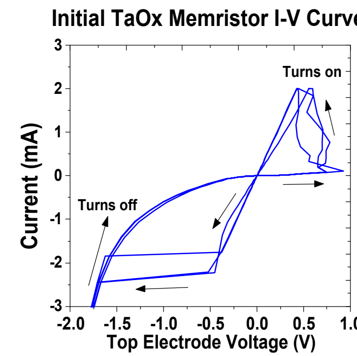
Field/Thermal induced Redox of insulator

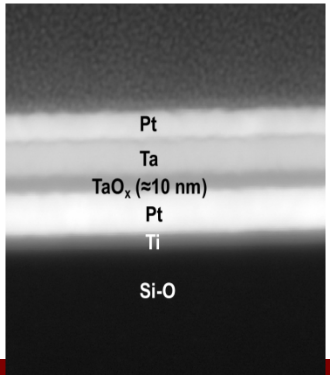
O- concentration and thermal gradients drive diffusion

Conductivity increases when O leaves nanocores due to Soret effect

Resistivity increases when O returns to nanocores due to dC/dx diffusion







The best initial composition is currently thought to be Ta_2O_4

Continuous electrical tuning of chemical composition of TaOx-based memristors

Feng Miao, Wei Yi, Ilan Goldfarba), J. Joshua Yang, M.-X. Zhang, Matthew D. Pickett, John Paul Strachan, Gilberto Medeiros-Ribeiro, and R. Stanley Williams**
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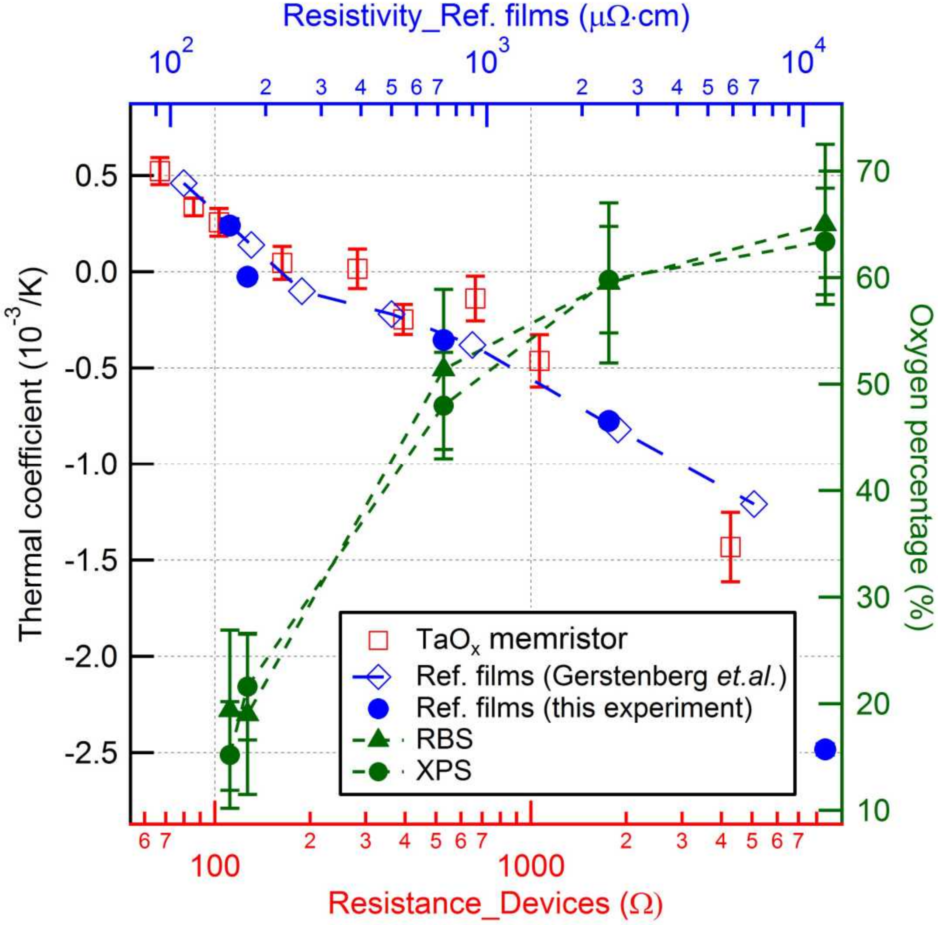
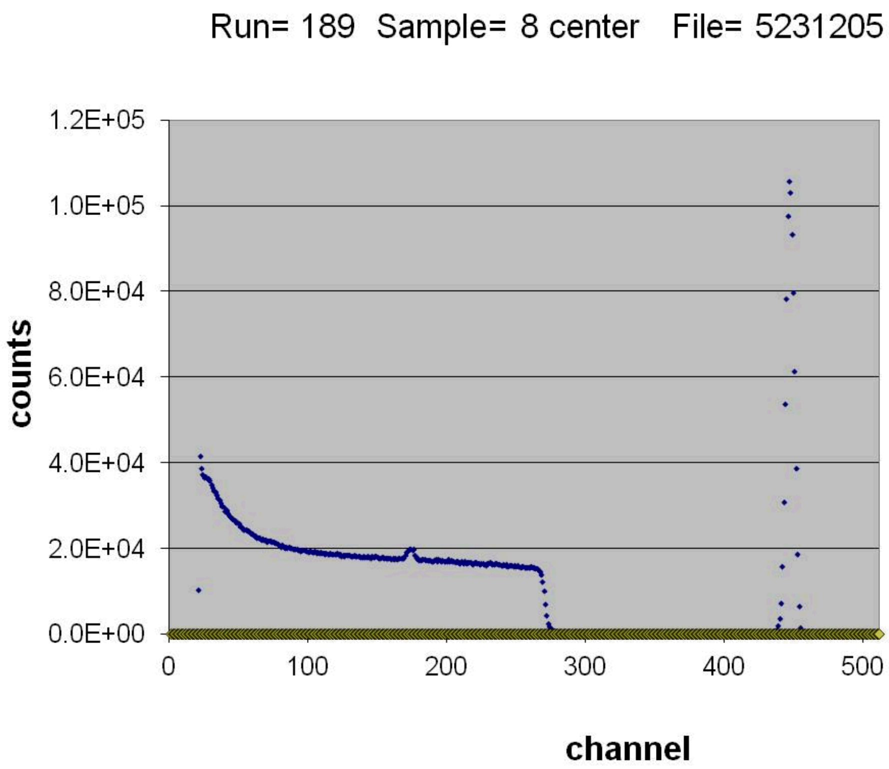
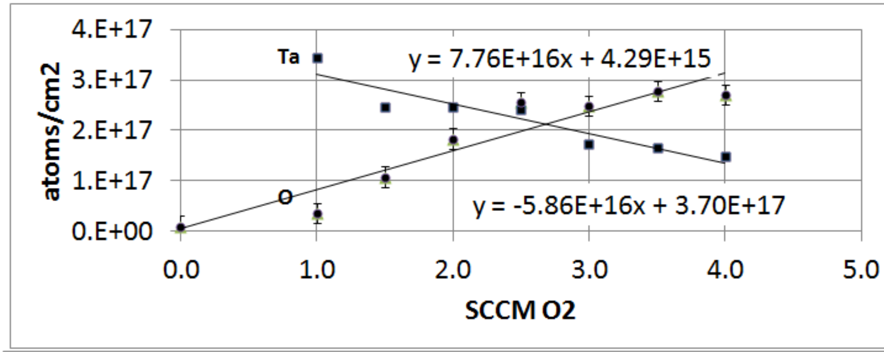


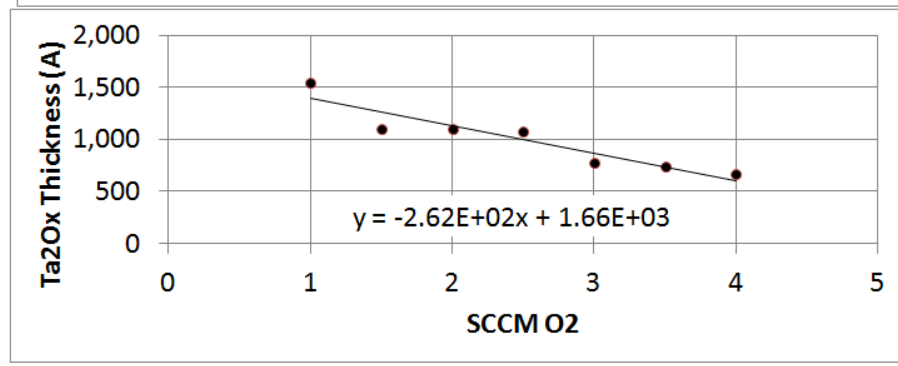
2 MeV He RBS of Ta2O5-x

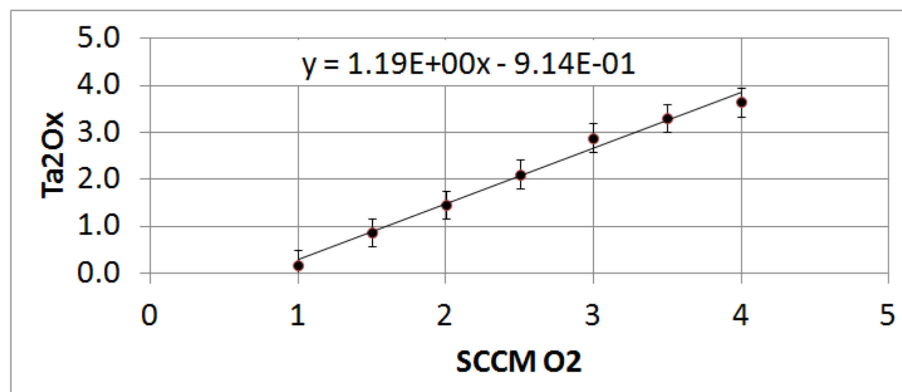


RBS
$$\sigma_{h,l} = \left[\frac{Z_p Z_{h,l} e^2}{4E}\right]^2 \frac{4}{\sin^4 \frac{\theta}{2}} \frac{\left[\cos\theta + \sqrt{1 - \left(\frac{M_p}{M_{h,l}}\sin\theta\right)^2}\right]^2}{\sqrt{1 - \left(\frac{M_p}{M_{h,l}}\sin\theta\right)^2}}$$
$$\frac{AD_l}{AD_h} = \frac{Y_l}{Y_h} \cdot \frac{\sigma_h}{\sigma_l}$$

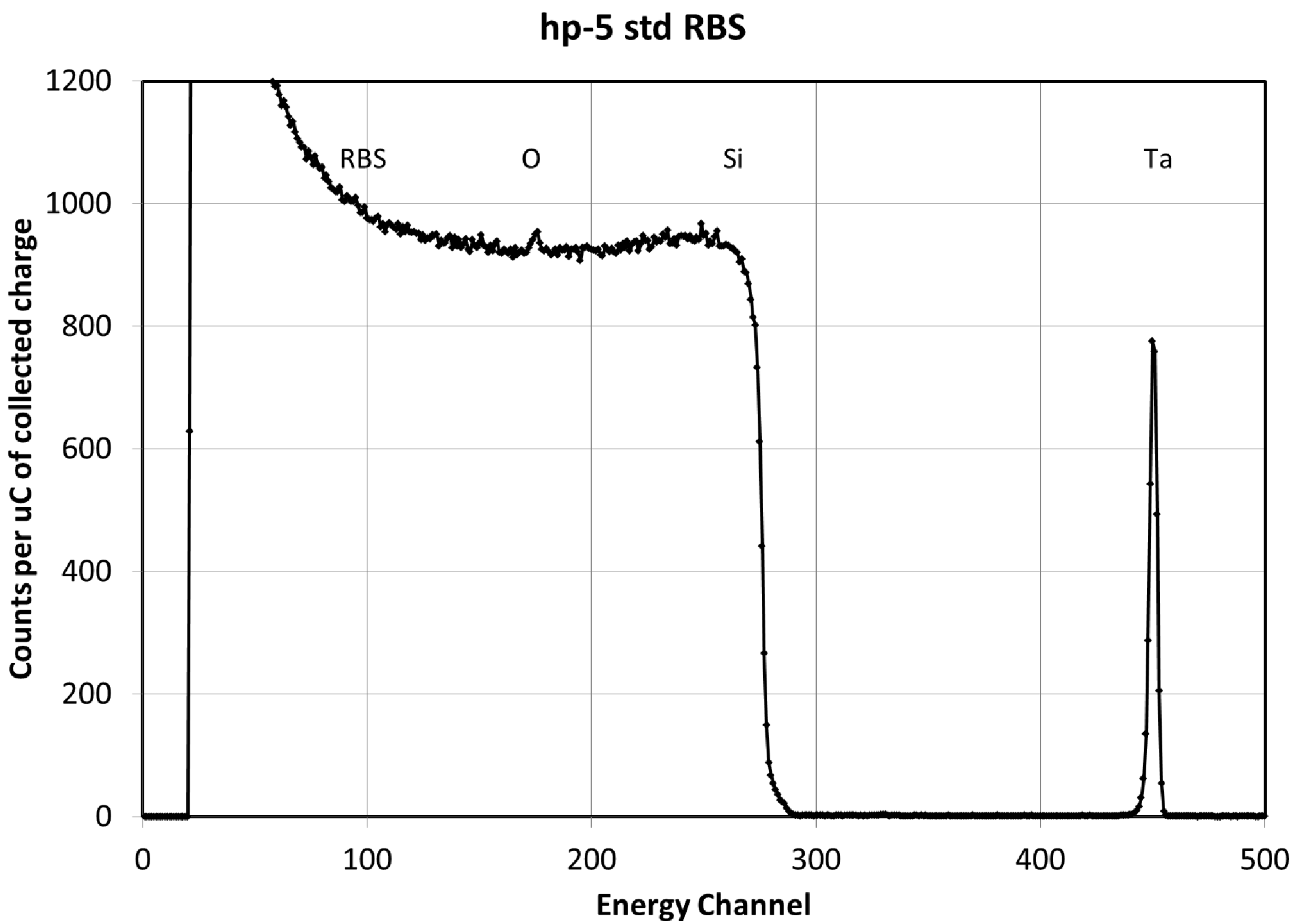
2 MeV He RBS provides adequate results for TaO films >50nm and is being used to calibrate the PVD systems used to grow the memristive films at SNL and HP.



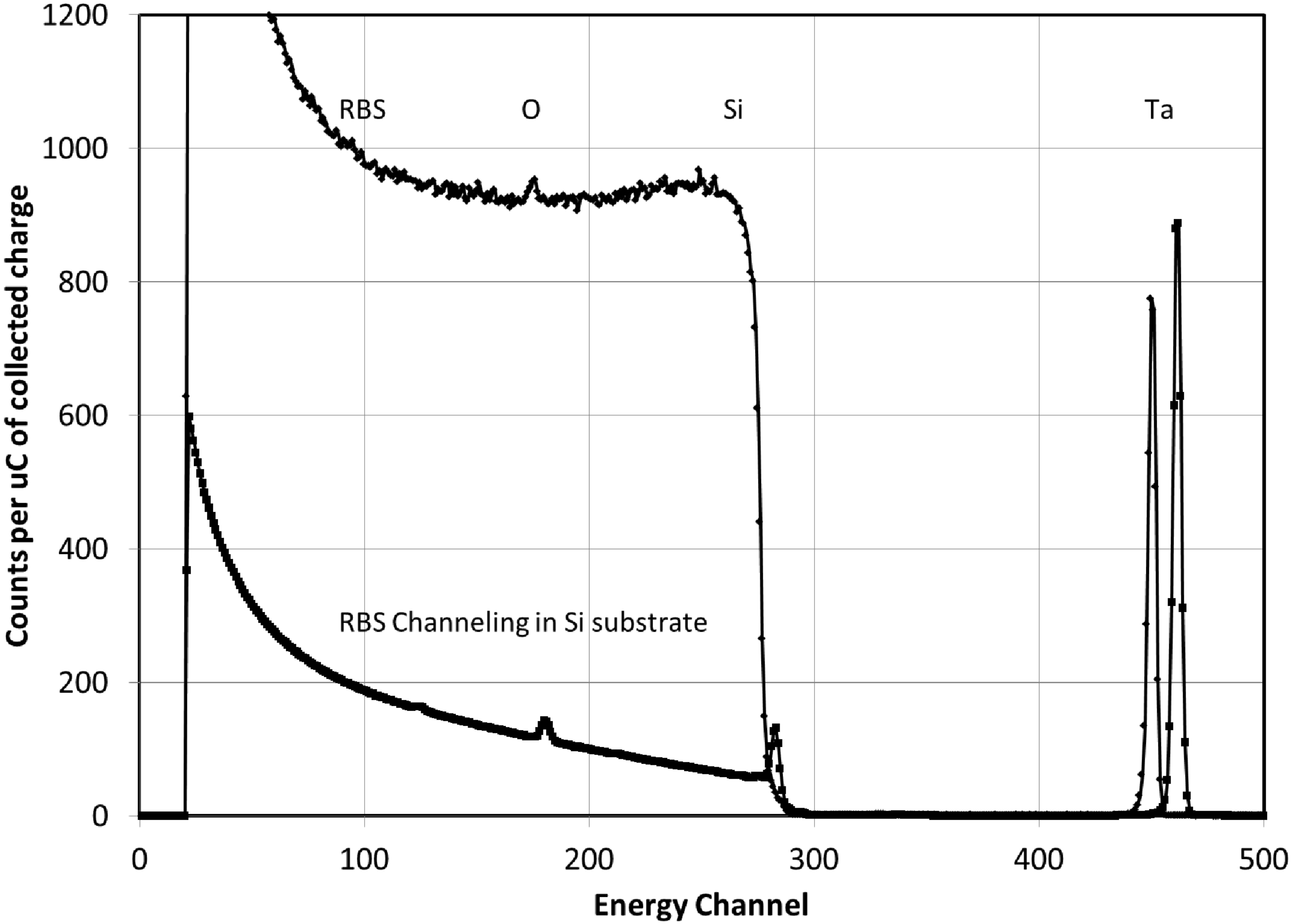




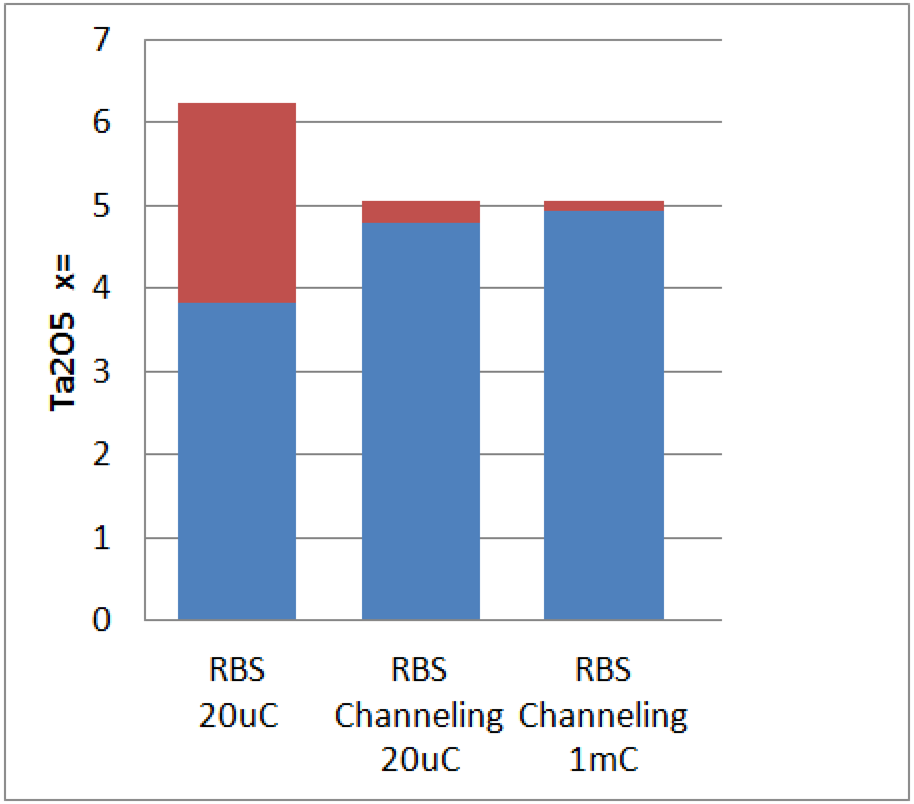
but some of the films are < 50nm, with some of the memristor layers being <10nm. These are very difficult to accurately measure using standard RBS.



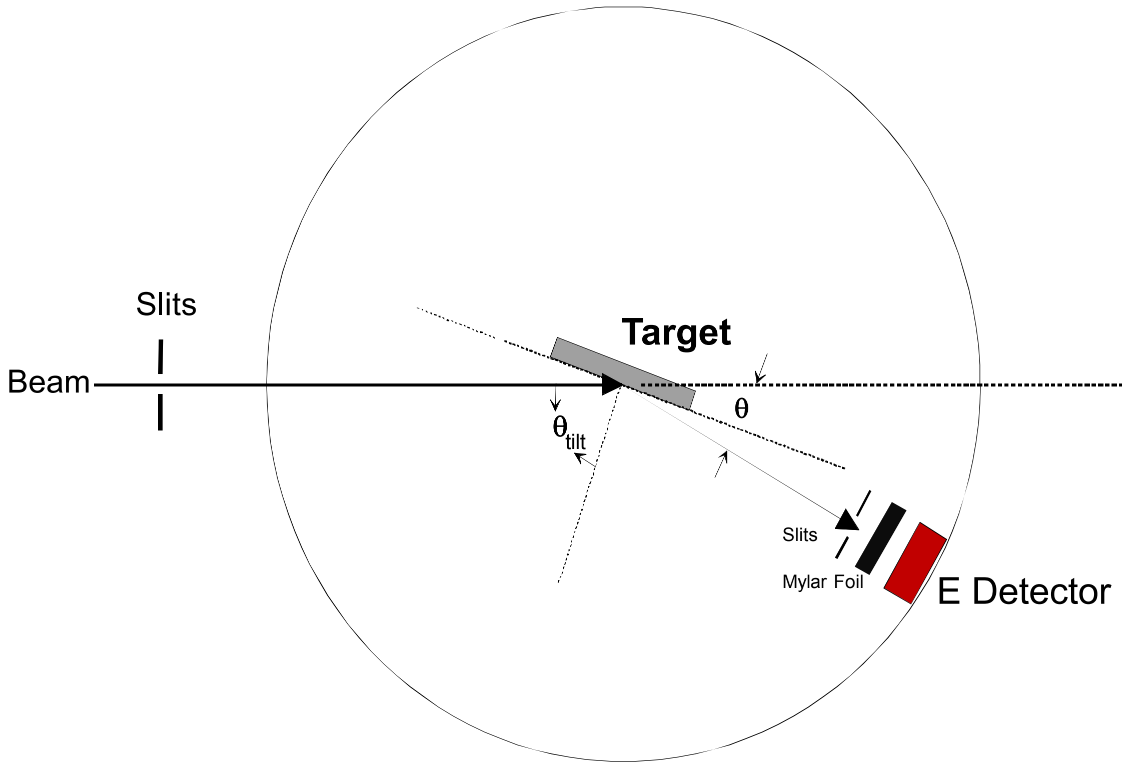
2 MeV Channeling RBS improves the signal to background considerably



, but is more complicated and takes very long runs to acquire adequate statistics.

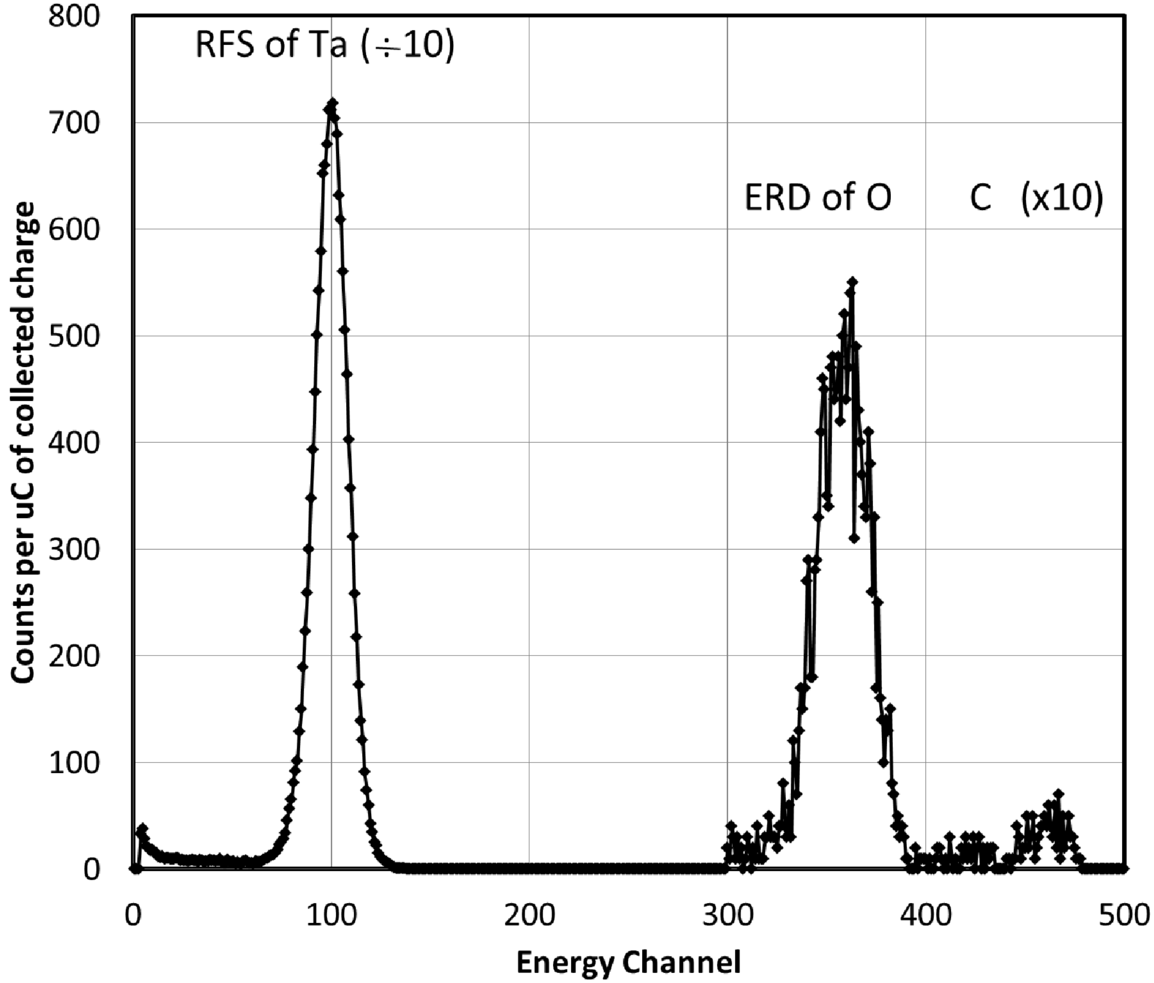


…so why not just use a standard heavy ion ERD system, and increase the Si (our preferred ERD beam) energy so that O recoils (ERD) and the Si that forward scatters (RFS) from the TaO_x transmits through the Mylar range foil, but the RFS from the Si substrate does not?



Scan of Si energy in standard ERD system

A more uniform Mylar foil that was 13.5 microns thick was then used with an increased Si energy of 42.5 MeV



The same approach is used to calculate areal density ratios for RBS and RFSERD, using the thin target approximation

RBS	RFSERD
$\sigma_{h,l} = \left[\frac{Z_p Z_{h,l} e^2}{4E}\right]^2 \frac{4}{\sin^4\frac{\theta}{2}} \frac{\left[\cos\theta + \sqrt{1-\left(\frac{M_p}{M_{h,l}}\sin\theta\right)^2}\right]^2}{\sqrt{1-\left(\frac{M_p}{M_{h,l}}\sin\theta\right)^2}}$	$\sigma_l = \left[\frac{Z_p Z_l e^2 (M_p + M_l)}{2M_l E}\right]^2 \cos^{-3}\theta$ $\sigma_h = \left[\frac{Z_h Z_p e^2}{4E}\right]^2 \sin^{-4}\left(\frac{\theta}{2}\right)$
$\frac{AD_l}{AD_h} = \frac{Y_l}{Y_h} \cdot \frac{\sigma_h}{\sigma_l}$	

But are the cross sections for 42.5 MeV Si on Ta and O still Rutherford?

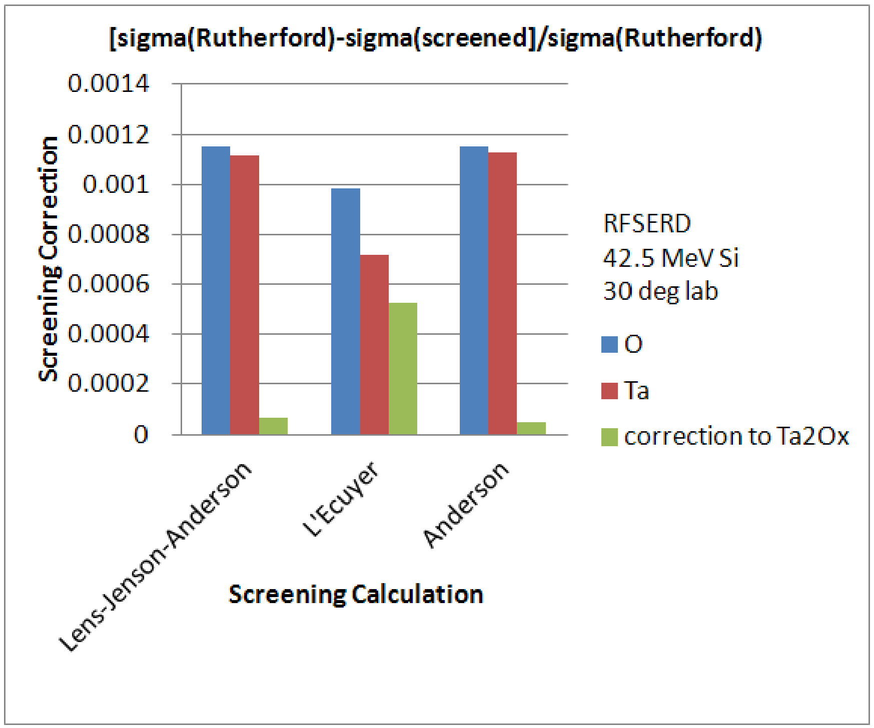
YES!! 42.5 MeV Si on O and Ta is still Rutherford, Screening only effects the 42.5 MeV Si on Ta and O by ~0.1%.

PHYSICAL REVIEW C VOLUME 29, NUMBER 1 JANUARY 1984

Elastic scattering phenomenological analysis of the first resonant structure of the $^{28}Si + ^{16}O$ system

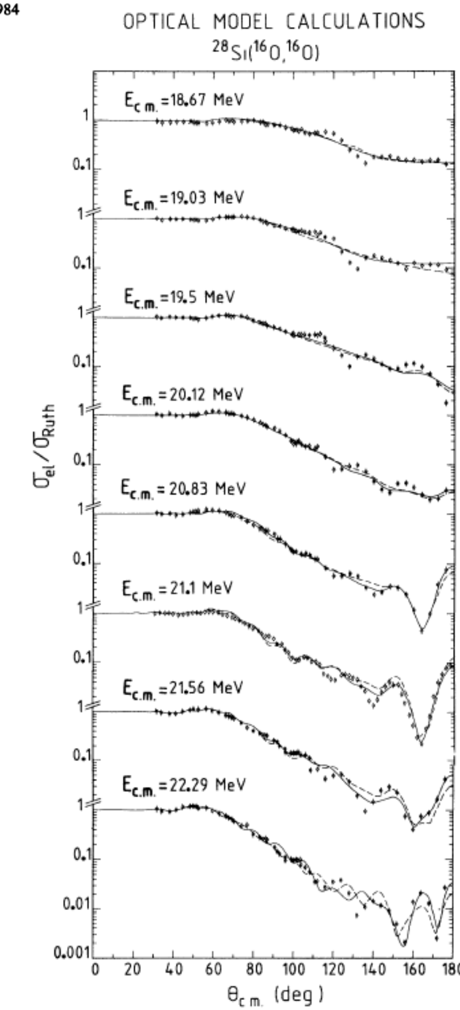
M. C. Mermaz, E. R. Chavez-Lomeli, J. Barrette, B. Berthier, and A. Greiner
Département de Physique Nucléaire/Basse Energie, Saclay, 91191 Gif-sur-Yvette Cedex, France

(Received 27 June 1983)

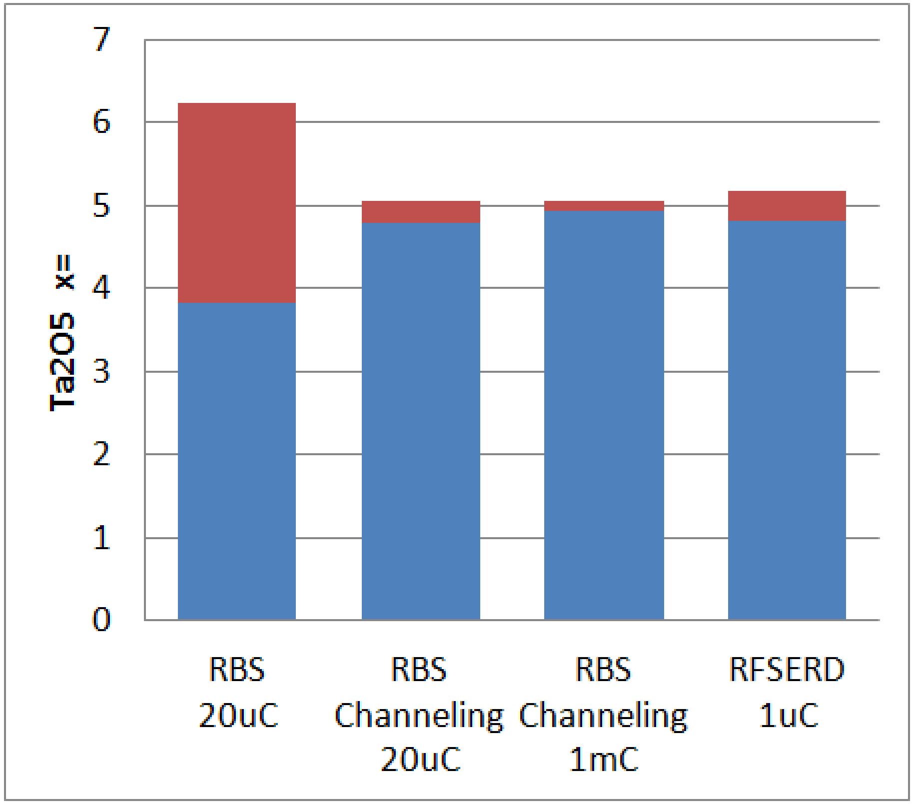


42.5 MeV Si on O is 15.45 MeV in the center of mass system

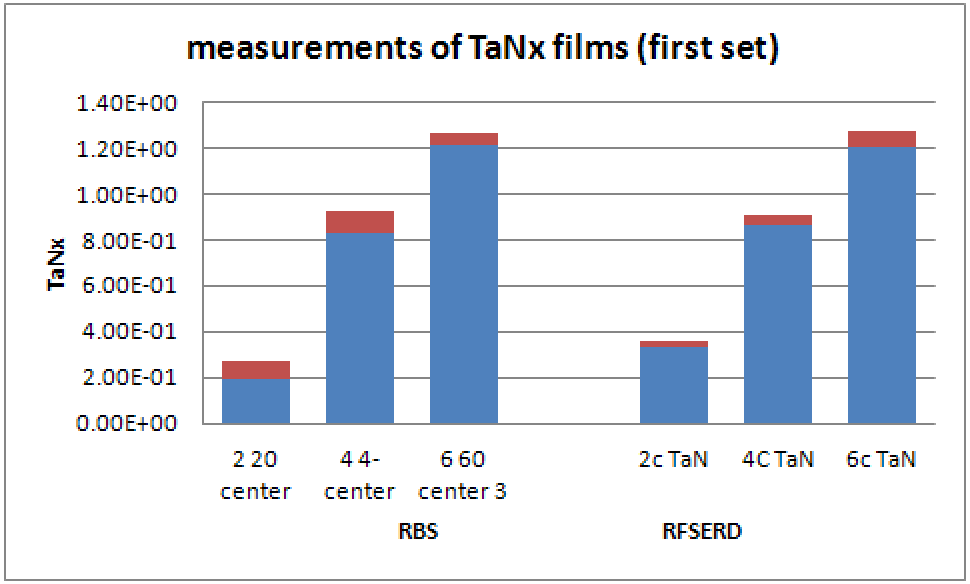
The Coulomb barrier for Si on Ta is Vcb ~ $Z_1 Z_2 /(A_1^{1/3} + A_2^{1/3})$ or 119 MeV in the com. So there should be no nuclear effects for this system as well.



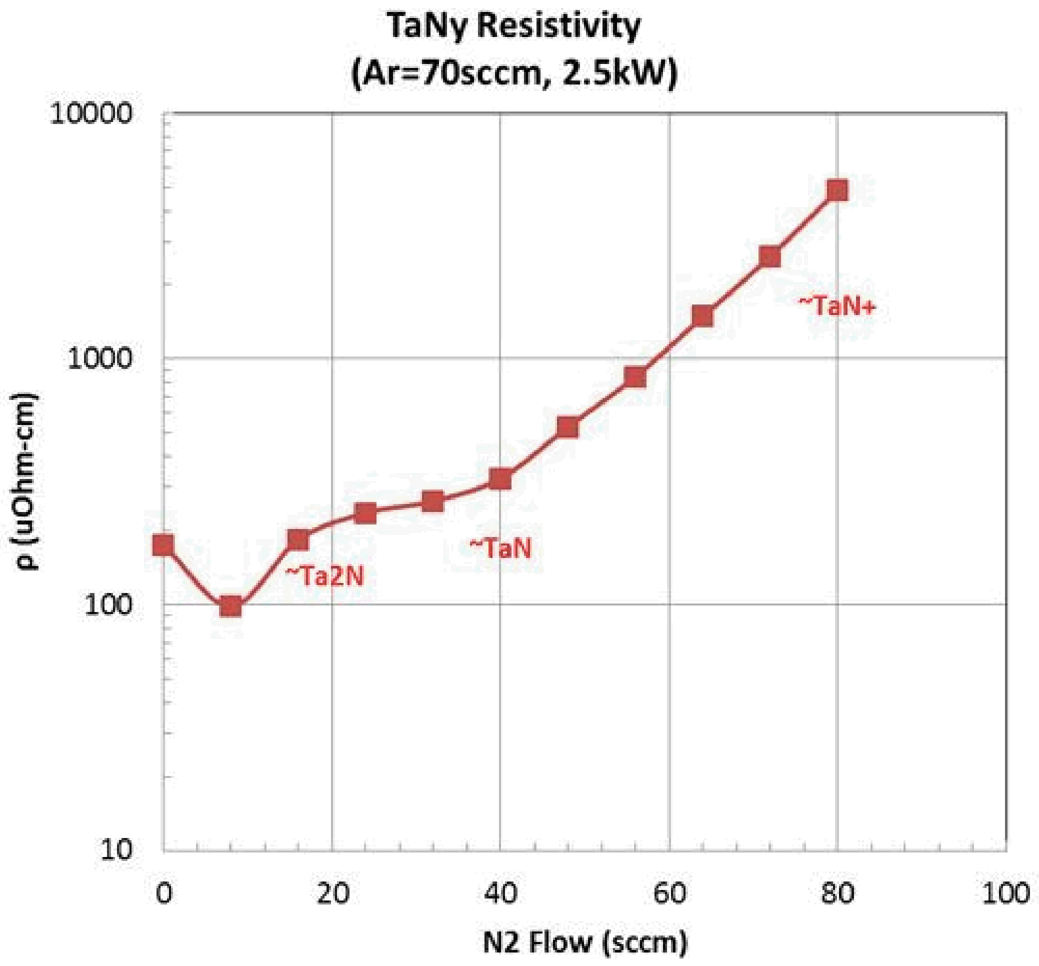
…so given that we can use Rutherford's equations for both the RFS and ERD, the areal density ratios can be easily calculated from the earlier equation, and converted into x composition values for the ultra thin Ta2Ox that is of interest for memristors.



…and RFSERD measurements have even started on ultra thin films of TaN films



TaN

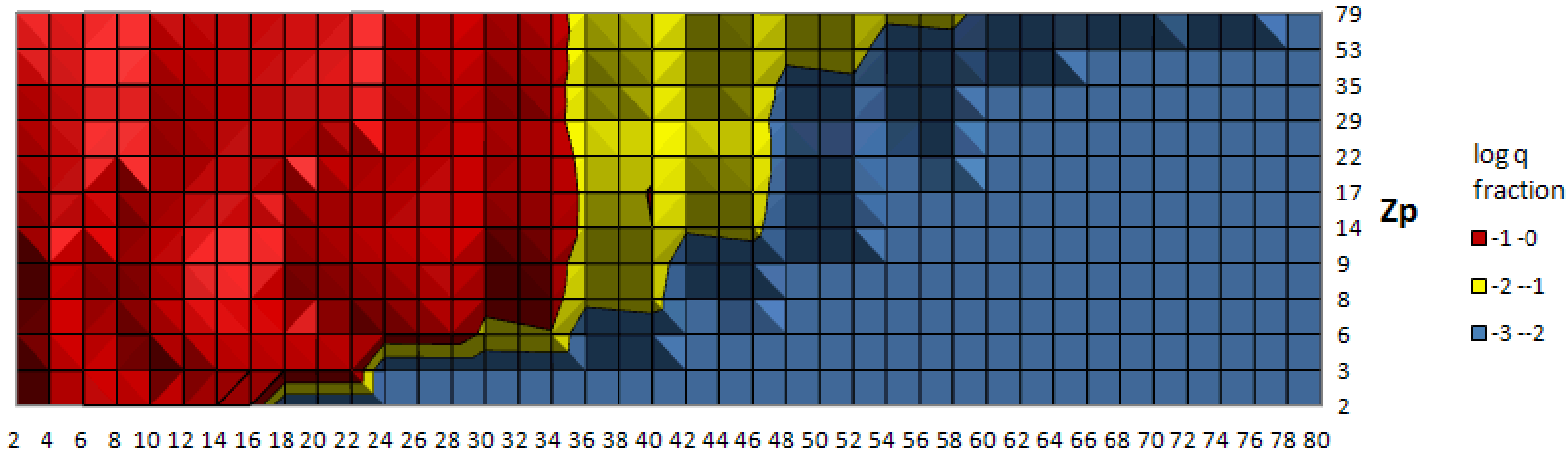

TaNy Resistivity
(Ar=70sccm, 2.5kW)
10000
1000
100
10
ρ (uOhm-cm)
~Ta2N
~TaN
~TaN+
0
20
40
60
80
100
N2 Flow (sccm)

ISSUES with RFSERD

- But are ~40 MeV Si ions optimum for performing RFSERD on systems like TaOx using tandems?

The maximum energy beams from a 6MV tandem with charge state fractions > 1%, and therefore adequate for the analysis, can be calculated using the Sayer theory.

Log of charge state fractions of maximum beams from Tandem with TV<6 MV, gas stripping and useable bending power of Magnets

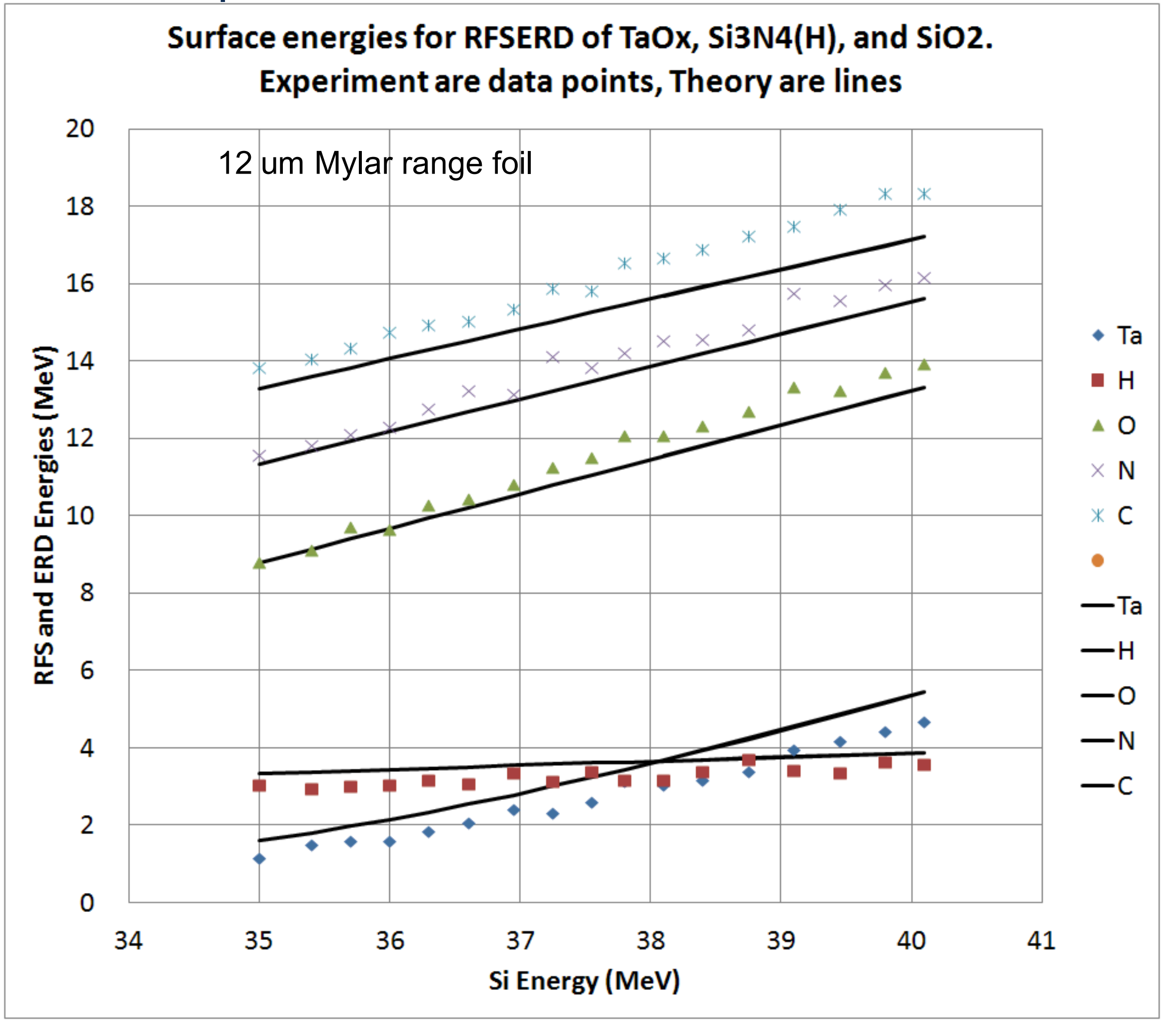


Z	q	TV	Emax f>1%	f
2	2	6.00	18	42.2%
3	3	6.00	24	36.8%
6	5	5.67	34	6.0%
8	6	5.71	40	1.8%
9	6	5.71	40	3.1%
14	7	5.75	46	1.4%
17	7	5.75	46	1.8%
22	7	5.75	46	1.9%
29	7	5.75	46	1.5%
35	7	5.75	46	2.0%
53	8	5.78	52	1.4%
79	9	5.80	58	1.2%

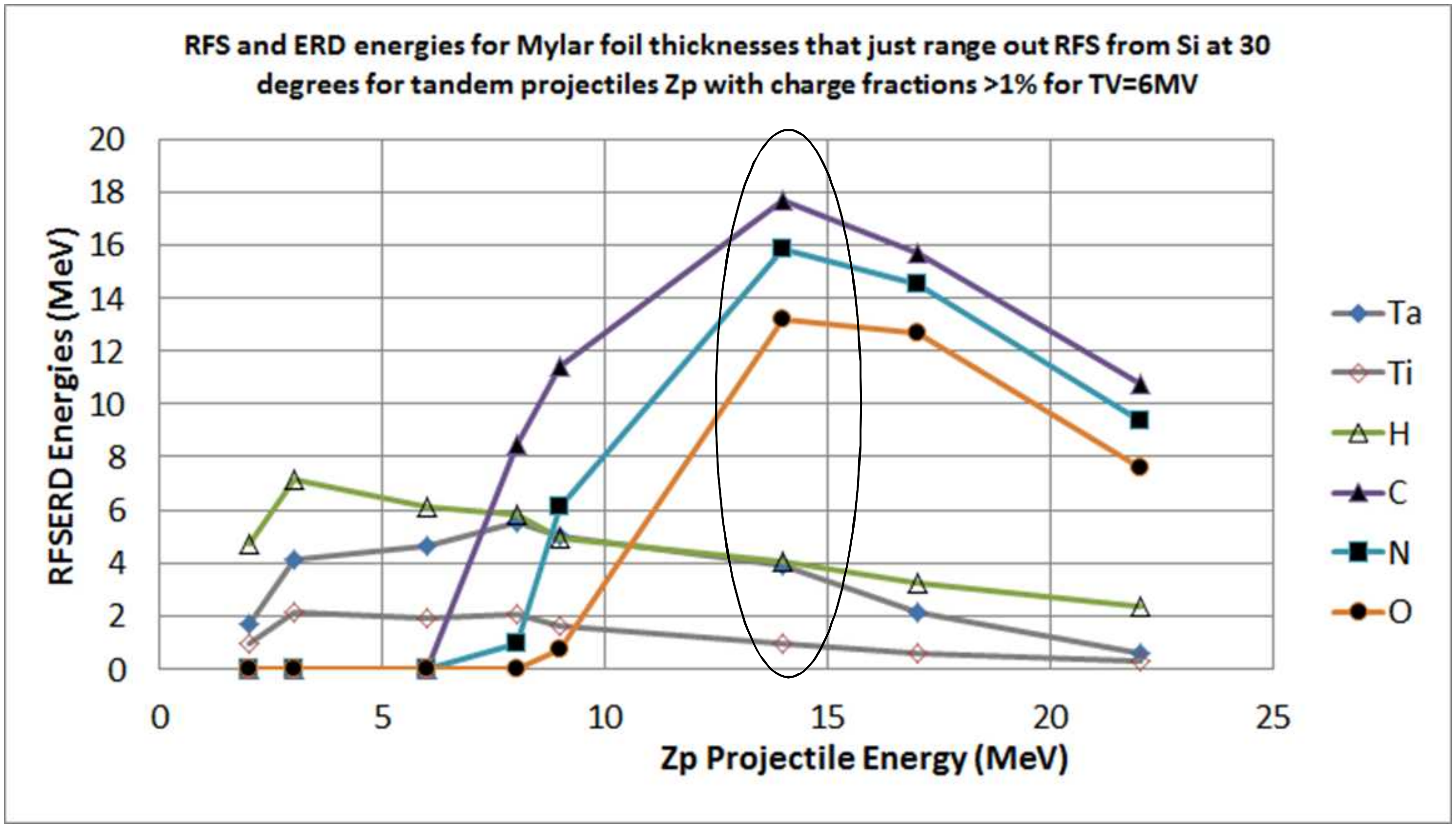
Optimum charge state Transmission factors for tandem ions.
As function on Z, velocity and maximum terminal voltage and max ME/Q2.

Fits from RO Sayer, Rev. de Phys. App. 12 (1543) 1977.

An excel program was developed that theoretically calculates the energies of both the scattered and recoiled ions following passage thru the range foil for the case of every combination of heavy and light atoms in the sample.

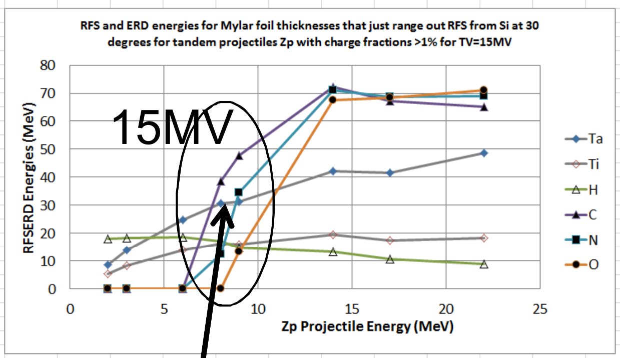


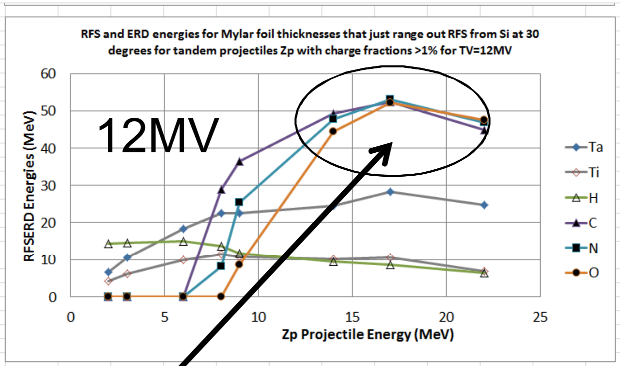
… and Si turned out to be the best!

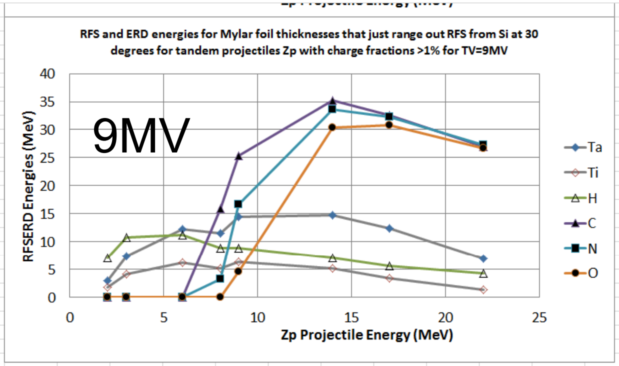


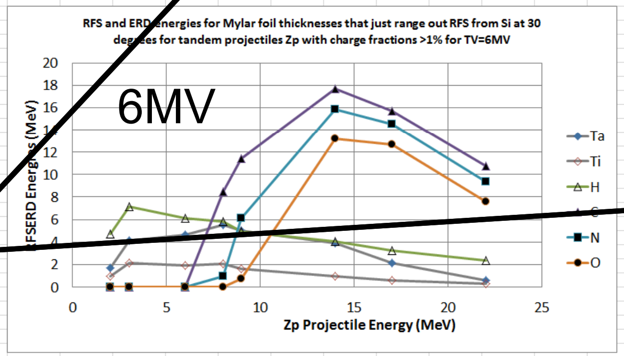
…and Si ions at ~40 MeV are also optimum

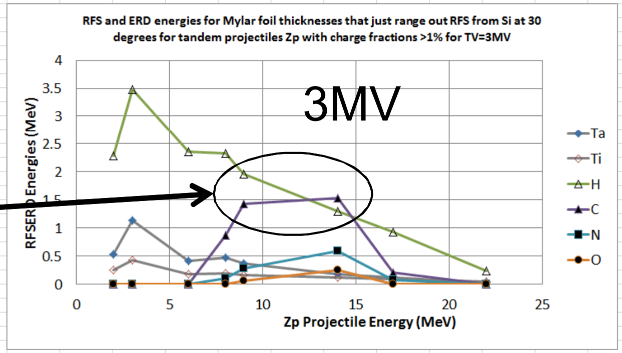
- To review: calculations were done for highest energy standard gas-stripped tandem ions with charge fractions >1% at an RFSERD angle of 30 degrees for RFS off Ti and Ta, and ERD of H, C, N and O.











- Ions with Z<14 result in overlaps of RFS and ERD energies
- For TV=3MV all of the signals have energies that are too low except for H and C
- With TV>6MV the ERD signals overlap for C,N,O

ISSUES with RFSERD

- Are ~40 MeV Si ions optimum for performing RFSERD on systems like TaOx using tandems?
  - YES!
- The RFS cross section is rapidly changing with scattering angle. How big is this effect, and does it compromise the measurement of areal density ratios?

These are first order approximations, that have been shown to be quite accurate when compared to exact calculations, of the sensitivity of the fractional error in the areal density ratios of light to heavy constituents in a sample using both RBS and RFSERD.

RBS	RFSERD
[illegible]	[illegible]
[illegible] (equation spanning both columns)	
[illegible]	[illegible] cos [illegible] / sin [illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible] for He RBS of Oxides	[illegible]

ISSUES with RFSERD

- Are 42.5 MeV Si ions optimum for performing RFSERD on systems like TaOx using a 6MV tandem?
  - YES
- The RFS cross section is rapidly changing with scattering angle. How big is this effect, and does it compromise the measurement of areal density ratios?
  - A rule of thumb is that the fractional error in % of the areal density ratio, is just the error in setting the scattering angle in degrees x10.
    - This angular accuracy is not attainable on most IBA-ERD systems except those used for ion channeling.
  - For RBS of oxides this % error is x0.1 this angular error in degrees!
  - … and necessitates the need for accurate heavy-light atom ultra thin film standards.

Future Work

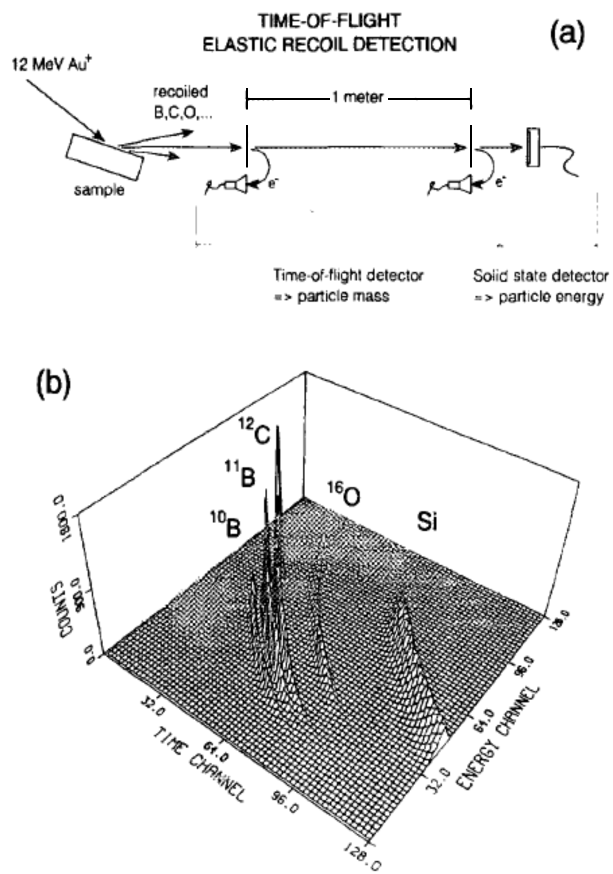
- 2 MeV He RBS will continue to be used to measure the stoichiometry of the TaOx films made at Sandia when the thickness is >100nm
- Films less than this thickness will be measured with RFSERD, but using the Ta2O5 HP standard
- And are starting microbeam experiments to test the single event upset sensitivity of memristors, and to pinpoint where these devices set or reset themselves due to total ionizing dose.
- We are considering bringing the TOF-ERD system back into operation to measure the concentration profiles of the Ta2O5 memristor stacks using 12 MeV Au ions.
  - … or collaborate with another lab that has TOF-ERD (see me later!)
  - Very interesting to profile the O with nm resolution to observe switching
- … and if anyone here wants to develop RFSERD, I would be glad to calculate the optimum beam, mylar thickness etc. for you.

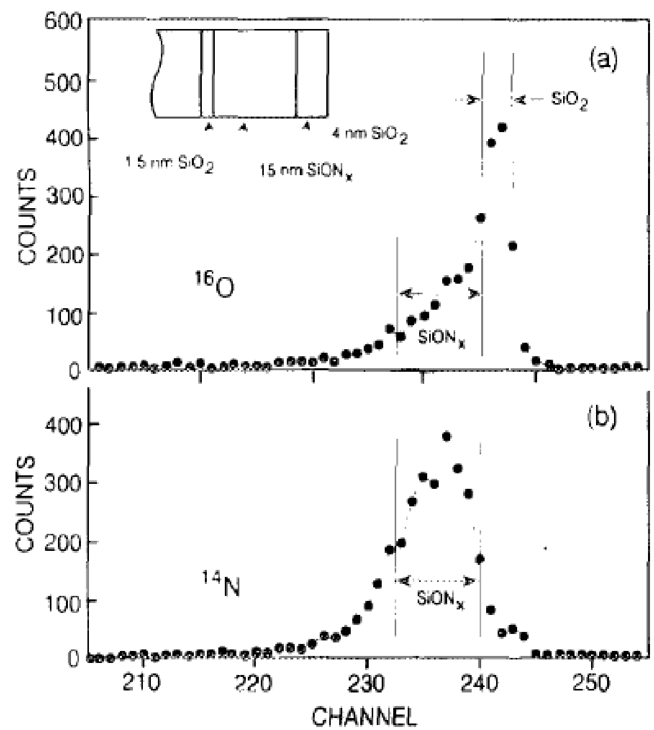
* Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

TOF-ERD would be a great technique using Au projectiles that would be kinematically filtered from being detected, but the SNL system was taken out of operation.

Knapp, Barbour, and Doyle: Ion beam analysis for depth profiling

J. Vac. Sci. Technol. A 10(4), Jul/Aug 1992 0734-2101/92/042685-06$01.00 2685





…and finally, a message to the students

- Even though IBA has been around for 50, and some would argue 100, years…
- It is still possible to find new ways to analyse materials by using ions!
- And even for cases where the technique isn't really new, its still possible to advance approaches to analysing the data.
- And the same is true in areas of materials modification, implantation, radiation effects simulations, …all using ions.
- I think this will always be the case!


720

There is strong evidence for these nanocores

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Anatomy of a Nanoscale Conduction Channel Reveals the Mechanism of a High-Performance Memristor

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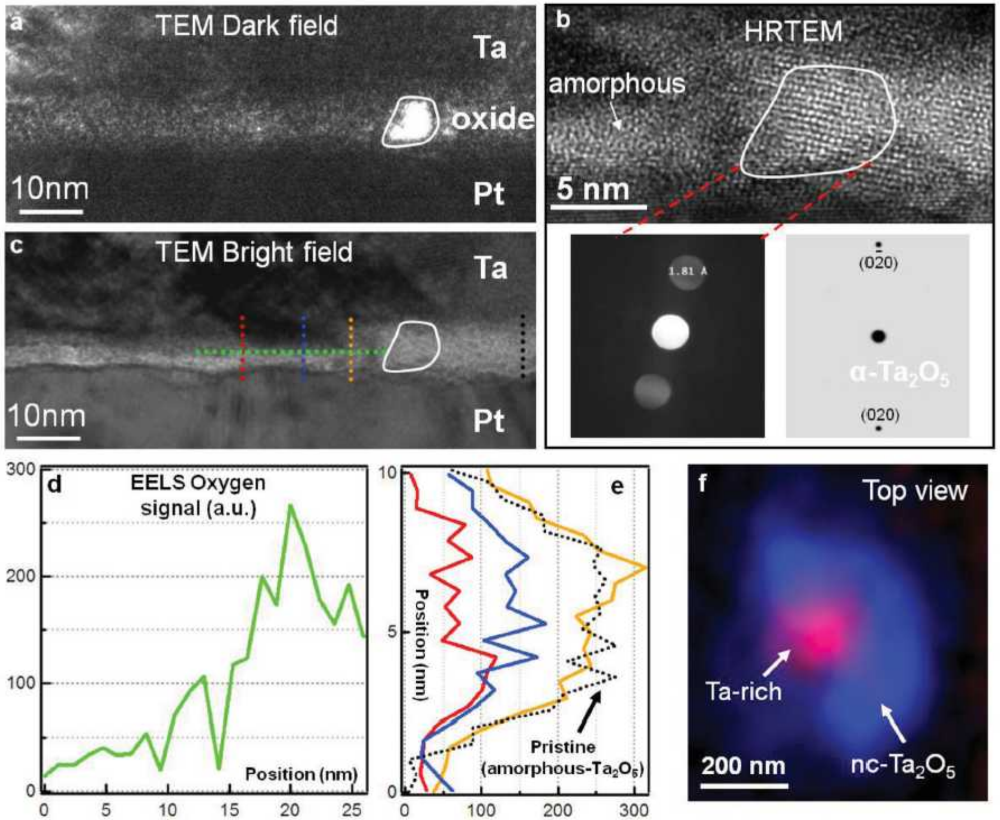

... and the magnitron sputtering system in the MESA-fab used to form TaOx memristive devices.