

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

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Abstract:

We present a novel ion beam analysis technique combining Rutherford forward scattering and elastic recoil detection (RFSERD) and demonstrate its ability to increase efficiency in determining stoichiometry in ultrathin (5-50 nm) films as compared to Rutherford backscattering. In the conventional forward geometries, scattering from the substrate overwhelms the signal from light atoms, but in RFSERD, scattered ions from the substrate are ranged out while forward scattered ions and recoiled atoms from the thin film are simultaneously detected in a single detector. The technique is applied to tantalum oxide memristors but can be extended to a wide range of materials systems.

Keywords: Rutherford Backscattering, Elastic Recoil Detection, Memristors,

1. Introduction:

As a result of continued miniaturization in pursuit of cost and performance benefits, many applications for materials and devices are emerging with a need for accurate stoichiometric control in ultra-thin films (often in the 3 to 20 nm range) where examples can be found in nearly all fields. We highlight here occurrences in our work toward developing valence change resistive memories, also known as memristors, which have become a likely candidate for next generation computer memory^{1,2}. In valence change resistive memory devices, standard voltages (1-3 V) generate large electric fields across a transition-metal oxide resulting in ion motion and a change in valence state within the device which corresponds to a change in electrical resistance. Specifically our interest is in creating sub-stoichiometric tantalum oxide (Ta_2O_x) films that are thin enough ($\sim 5\text{-}20$ nm) to generate extreme electric fields

and simultaneously have precise stoichiometric control such that electrical resistance across the device can be significantly and reversibly altered by the changing valence state. Additionally the electrodes need to be of a similar thickness and for, CMOS compatibility, a preferred material is tantalum nitride which has conductivity that varies over orders of magnitude for relatively small changes in nitrogen to tantalum ratio. The analytical challenge is therefore clear: develop a technique that can accurately measure the stoichiometry of nm-thick films of Ta_2O_x and TaN_x .

2. Materials and Methods

Precise thickness and compositional control of the deposition of sub-stoichiometric Ta_2O_5 films is critical in order to produce the required oxygen vacancies in valance change memristive devices³. The films studied here were deposited using PVD reactive sputtering⁴ on witness coupons of 001 Si substrates that had the usual 1.5 nm SiO_2 surface layer.

2.1. RBS and Channeling RBS

These types of films are usually too thick (up to 5-50 nm) for most surface characterization techniques such as X-ray photoelectron spectroscopy or Auger electron spectroscopy. Also, the non-destructive nature of ion beam analysis is a significant advantage but these films are also usually too thin for Rutherford backscattering (RBS) to be efficient. For ultra-thin samples, backscattering from the silicon substrate overwhelms the small signal generated from lighter atoms, in our case the oxygen and nitrogen atoms in TaO_x and TaN films respectively. For cases like those studied here, where the film has different crystallinity than the substrate, channeling can be used to reduce the relative signal contribution from the substrate. Unfortunately, despite the increased signal to noise ratio, total charge collection required for sufficient statistics makes RBS prohibitively slow and having to find the optimal sample orientation for channeling makes it too complex and time consuming. In some materials systems it is possible to simply increase the incident He ion beam energy until scattering from the low energy atom becomes non-Rutherford⁵, thereby increasing its signal above the background. Unfortunately a different approach must be used for silicon substrates, which are ubiquitous in microelectronics, because He scattering from Si also becomes highly non-Rutherford⁶ at relatively low energy. It may also be possible to analyze these films using gas ionization

detection of recoiled atoms⁷ or time-of-flight elastic recoil detection⁸ (TOF-ERD) but neither experimental system is currently available at Sandia.

Fig. 1 shows the signal collected from a 5 nm Ta₂O₅ film using 2 MeV He ions using standard RBS and Channeling RBS. This data highlights the small oxygen signal that is detected above the Si substrate background. RBS techniques are too slow, even with improved signal from channeling, for thin films where the substrate background overwhelms the signal. The inset shows the analysis of these spectra.

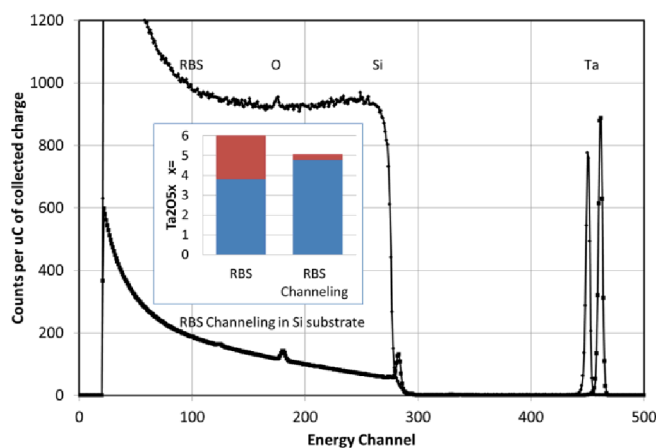


Fig. 1. Signal collected from a 5 nm Ta₂O₅ film using 2 MeV He ions using standard RBS and Channeling RBS. The inset shows the analysis of these spectra.

2.2 RFSERD

We propose here an alternative scattering approach that utilizes simultaneous detection of elastically recoiled light atoms and Rutherford forward scattering from heavy elements in the film at a single detector while ranging out forward scattered ions from the substrate. The specific geometry used in our experiment is shown in Fig. 2 where the scattering angle is 30 degrees with a 75 degree tilt. Scattering cross-sections can be calculated based on Rutherford formula from which relative areal densities can be easily computed to give stoichiometry:

[2]

[3]

In the above equations, q is electric charge and σ_{H} and σ_{L} represent scattering cross-sections of forward scattering from heavy elements and recoil of lighter elements respectively. Z_p , Z_H , and Z_L correspond to atomic numbers of the projectile, heavy and light atoms with the same subscript notation for A corresponding to atomic mass. The scattering angle is denoted by θ (note that the lab scattering angle can be used here and only a 0.1% error results) and θ_{H} , θ_{L} and θ_{H} , θ_{L} correspond to areal density and yield for heavy and light atoms respectively.

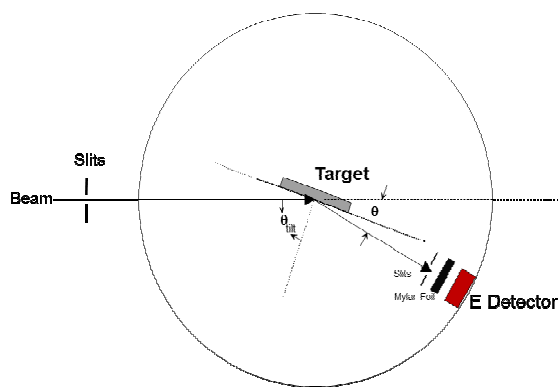


Fig 2: Experimental geometry of RFSEED.

Determining the optimal projectile ion and beam energy involves ensuring that the elements of interest (e.g. Ta, N and O for our case) are sufficiently separated in energy for both ERD and RFS and that their signals are within an easily detectable energy range. Using the Sayer theory⁹ of charge state fractions emitted from the terminal of a gas-stripped tandem accelerator, it is possible to estimate the maximum energy beam for charge populations greater than 1%, and therefore useful for IBA, for varied projectiles and terminal voltages. From the maximum energy values, the minimum thickness of Mylar foil required to just range out Si atoms originating in the substrate can be calculated using the ZBL stopping power theory¹⁰. In Table 1, such calculations have been made for tandem accelerators with maximum terminal potentials of 3, 6, 9, 12 and 15 MV.

max TV (MV)	Zp	E (MeV)	Mylar (um)
3	2	6	34.7
	3	12	38.8
	6	12	11.8
	8	15	10.2
	9	15	9.2
	14	15	7.7
	17	15	8.7
	22	15	14.0
6	2	12	106.9
	3	24	109.1
	6	30	33.6
	8	36	24.6
	9	36	19.9
	14	42	13.3
	17	42	11.7
	22	42	12.3
9	2	18	213.7
	3	36	211.7
	6	54	76.9
	8	54	40.8
	9	63	38.3
	14	72	21.5
	17	72	16.7
	22	72	14.0
12	2	36	726.2
	3	48	344.9
	6	72	119.5
	8	84	75.4
	9	84	56.0
	14	96	29.1
	17	108	23.8
	22	108	17.1
15	2	45	1083.9
	3	60	507.8
	6	90	170.5
	8	105	105.0
	9	105	76.4
	14	135	43.2
	17	135	29.8
	22	150	21.5

Table 1. Maximum energies of projectiles useful for RFSEED on tandem accelerators are listed for terminal voltages ranging from 3 to 15 MV. Also listed are the thicknesses of Mylar required to range out the RFS signal from these projectiles scattering from a Si substrate.

Combining beam energies with range foil thicknesses listed in Table 1, the energy of recoiled atoms and forward scattered ions at the detector can be easily calculated using the standard kinematics relationships and ZBL stopping powers of the RFSERD ions passing through Mylar. Recoiled atom energies were calculated for elements from hydrogen to fluorine for the range of projectile and terminal voltage combinations adjusted for range foil thickness. For visual simplicity, Fig 3 shows the resulting energies for only the elements nitrogen and oxygen which are particularly relevant for valence change memory applications. Also in Fig 3, the energy at the detector is shown for forward scattered ions from tantalum, which is also particularly relevant in our case.

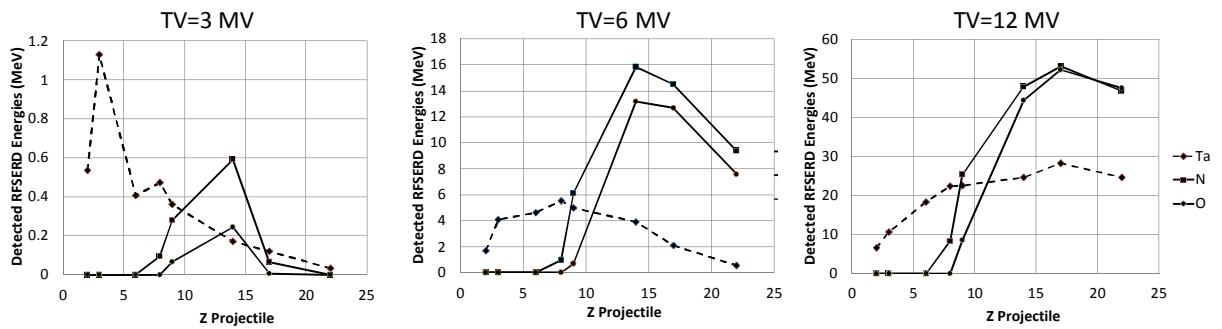


Fig. 3. Detected energies for forward recoiled N and O (solid lines), and ions scattered by Ta (dashed lines) at 30° for the maximum energy projectiles and minimum Mylar foil thicknesses listed in Table 1 for gas stripped tandems with terminal voltages of 3, 6 and 12 MV.

Considering the energies of the detected particles, it is possible to identify suitable projectile and terminal voltages. For low terminal voltages (3 MV) the detected energies are too low to be easily applicable. For higher terminal voltages (> 6 MV) the detected energies for carbon, nitrogen and oxygen start to overlap. Therefore 6 MV terminal voltage was deemed optimal for studying the Ta_2O_x on silicon system. For low Z projectiles (less than Si) the ERD and RFS energies overlap. For Z greater than Si, the energy spacing between elements of interest start to decrease and because of increased energy straggling may become overlapped. Therefore Si ions were selected as the projectile for evaluating the TaO_x valence change memory materials.

It should be noted that although the configuration demonstrated here is shown to be effective for accurately measuring stoichiometry in TaO_x films down to 5 nm and possibly thinner, other configurations may be preferred for samples containing different elements either in the film itself or the substrate. By employing the same process it is possible to determine the best configuration for alternate substrate-film combinations or for

identifying other elements within the same substrate-film combination. For example, while Si projectiles give good energy separation for the elements of interest in our study, a lighter projectile may be better suited for differentiating between carbon and lithium within the same sample. Additionally, the tantalum and hydrogen detected energies are not well separated for a Si projectile so a heavier projectile such as titanium may be better if both hydrogen and tantalum are to be detected.

3.0 Experiment and Discussion

With the Sandia EN tandem set at 6.07 MV, a Si beam with 42.5 MeV beam energy was obtained. From Table 1, this energy of Si requires a $\sim 13.5 \mu\text{m}$ Mylar foil at scattering angle of 30 degrees as shown in the geometry illustrated in Fig. 2 to stop the Si ions that scatter from the Si substrate. Based on the calculations above, this configuration should provide good energy separation between elements that are commonly of interest (Ta, N, and O), and selectivity against substrate signal.

An RFSEERD spectrum with the parameters described above is shown in Fig. 4. The sample being measured was the same 5nm thick Ta_2O_5 that was analyzed by RBS in Fig. 1. Note that the spectrum has been normalized for 1 μC of accumulated charge during the experiment, and that the RFS signal from Ta has been divided by 10, whereas the ERD signal from O (and C) has been multiplied by 10. Inserted in this spectrum is the analysis of the Ta_2O_x stoichiometry. In contrast to the RBS spectra in Fig. 1, the RFS from Ta is now at the lower energy and the ERD of O and some C is seen at the higher energies. But the main difference is the near absence of backgrounds. For the Ta RFS a small background is thought to be caused by multiple scattering of the Si from the Ta, and the background underneath the O ERD signal is most likely due to pile up.

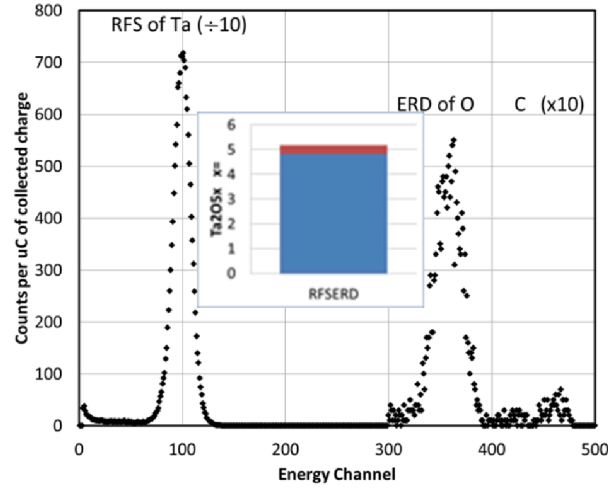


Fig. 4. RFSEED of 5nm Ta₂O₅ film on Si is shown. The inset shows the analysis of the spectrum where the red bar indicates the statistical spread.

RFSEED uses increased beam energy and varied projectile as compared to the conventional techniques (2 MeV He ions). It is therefore necessary to verify the absence of nuclear and screening effects prior to quantifying results. The screening effect was estimated for a 42.5 MeV Si beam at 30 degrees for oxygen, tantalum and tantalum oxide, using the L'Ecuyer¹¹ formula, and was found to be less than 0.12% which is well within the range needed for distinguishing stoichiometry-related performance variation¹² in memristive materials. At a Si beam energy of 42.5 MeV the recoil cross section for oxygen is still Rutherford¹³ and the Coulomb barrier for Si on tantalum can be calculated in the center-of-mass reference frame as $V_{CB} \sim e^2 Z_T Z_P / (A_T^{1/3} + A_P^{1/3})$ to be 119 MeV so equations 1-3 can be applied to give stoichiometry quantitatively but a reference sample is still required because of the technique's sensitivity to scattering angle as discussed below.

To quantify the sensitivity to incident angle in RFSEED we define a parameter F (Eq. 4) that is equal to the ratio of scattering cross sections of the forward scattering and recoiled elements (defined in Eqs. 1 and 2).

The differential in F with change in angle, normalized by the magnitude of F itself can be used to estimate the error in sensitivity of RFSEED as a function angle.

$$-\frac{1}{F} \frac{dF}{d\theta} = 3 \tan(\theta) + \frac{2}{\tan\left(\frac{\theta}{2}\right)} = 0.16 \text{ for } d\theta \text{ in degrees} \quad [5]$$

This means that the reproducibility in setting θ , the RFSEED angle, needs to be ~ 0.1 degree for a fraction error in the ratio of light/heavy areal densities to be 1.6%. For comparison, routine RBS on TaO_x is 100x less sensitive to backscatter angle reproducibility for the same fractional error. Stated another way, the angular accuracy needs to be approximately 100 times better in RFSEED than for conventional RBS. Attaining this level of scattering angle reproducibility is possible in systems designed with the channeling capability but is difficult for a system like the one in use at Sandia that was not designed for high angular sensitivity. As a result of the large angular sensitivity, standard samples are generally required for quantitative analysis, and the sample analyzed above is being used as such a standard based on an extremely long channeling RBS measurement, with 1mC of collected charge, to be $\text{Ta}_2\text{O}_{5\pm 0.1}$.

4.0 Conclusions:

In response to the need for precisely characterized ultrathin films containing both heavy and light elements we have developed a new ion beam analysis technique called Rutherford forward scattering and elastic recoil detection (RFSEED). The technique is able to remove the influence of the substrate signal that, in conventional RBS, makes detection of light elements difficult. Unfortunately, RFSEED is sensitive to angle and therefore necessitates experimental equipment designed for high angular sensitivity and standard samples. Compared to conventional RBS however, RFSEED enables a significant increase in efficiency, requiring reduced total charge collected while maintaining sufficient statistical accuracy in determining stoichiometry. The technique was demonstrated for the Ta_2O_x thin film on silicon material system that is of contemporary interest in electronic memories. Characterizing the stoichiometry of these films was greatly facilitated through the use of RFSEED, enabling the study of films down to 5 nm and possibly thinner via non-destructive ion beam analysis. While RFSEED is now in routine use in our memristor development program, it could find many other applications in materials analysis where ultrathin films of high and low mass elements are found. An Excel program has been

written that performed the calculations above, and can be made available to researchers in the IBA field who want to develop RFSEED in their labs.

5.0 Acknowledgements:

***Standard SNL-DOE.

¹ J.J. Yang, D.B. Strukov, D.R. Stewart, "Memristive devices for computing," *Nature Nanotechnology*, 8 p. 13 (2012).

² H.-S.P. Wong, H.-Y. Lee, S. Yu, Y.-S. Chen, Y. Wu, P.-S. Chen, B. Lee, F.T. Chen, M.-J. Tsai, "Metal-Oxide RRAM," *Proceedings of the IEEE*, 100 p. 1951 (2012).

³ Hopefully my paper about "Forbidden Region"

⁴ Hopefully Jim's Deposition Paper

⁵ J.C. Barbour, B.L. Doyle, S.M. Myers, "Measurement of the oxygen content in high-T_c superconductors: Enhanced resonant ion-scattering analysis", *Physical Review B* vol 38 num 10 p. 7005 (1988)

⁶ J.R. Tesmer et al, *Materials Chemistry and Physics* 46 p. 189-197 (1996).

⁷ H. Timmers, R.G. Ellman, T.R. Opiel, "Characterization of thin films using heavy ion beams", *Bulletin of Materials Science* Vol 22, No. 3, p. 601-606 (1999).

⁸ Knapp, Barbour, Doyle, "Ion beam analysis for depth profiling", *Journal of Vacuum Science and Technology A* 10 (4) (1992).

⁹ R.O. Sayer, "Semi-empirical formulas for heavy-ion stripping data", *Rev. de Phys. App.* No. 12, p. 1543-1546 (1977).

¹⁰ J.F. Ziegler, J.P. Biersack, U. Littmark, *The Stopping and Ranges of Ions in Matter* (Plenum, New York, 1985), Vol 1.

¹¹ L'Ecuier Screening THE IMPORTANCE OF SCREENING CORRECTIONS IN ACCURATE RBS MEASUREMENTS AT MEV ENERGIES Author(s): LECUYER, J; DAVIES, JA; MATSUNAMI, N Source: RADIATION EFFECTS AND DEFECTS IN SOLIDS Volume: 47 Issue: 1-4 Pages: 229-232

¹² F. Miao, W. Yi, I. Goldfarb, J.J. Yang, M.-X. Zhang, M.D. Pickett, J.P. Strachan, G. Medeiros-Ribiero, R.S. Williams, "Continuous electrical tuning of the chemical composition of TaO_x-based memristors," *ACS Nano*, 6 p. 2312 (2012).

¹³ M.C. Mermaz, E.R. Chavez-Lomeli, J. Barrette, B. Berthier, A. Greiner, "Elastic scattering phenomenological analysis of the first resonant structure of the ²⁸Si + ¹⁶O system