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XPS Investigation of Monatomic and Cluster Argon Ion Sputtering of Tantalum Pentoxide

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Highlights

- Ion beam induced oxide reduction from monatomic and gas cluster ion beam exposure are compared.
- Lower relative level of preferential sputtering is shown in gas cluster ion beam depth profiling.
- A lack of “steady state” is observed in gas cluster ion beam depth profiles of tantalum pentoxide.
- Possible mechanisms behind the observed results, including temperature effects are proposed.
Abstract

In recent years, gas cluster ion beams (GCIB) have become the cutting edge of ion beam technology to sputter etch organic materials in surface analysis. However, little is currently known on the ability of argon cluster ions ($\text{Ar}_n^+$) to etch metal oxides and other technologically important inorganic compounds and no depth profiles have previously been reported. In this work, XPS depth profiles through a certified (European standard BCR-261T) 30 nm thick $\text{Ta}_2\text{O}_5$ layer grown on Ta foil using monatomic $\text{Ar}^+$ and $\text{Ar}_{1000}^+$ cluster ions have been performed at different incident energies. The preferential sputtering of oxygen induced using 6 keV $\text{Ar}_{1000}^+$ ions is lower relative to 3 keV and 500 eV $\text{Ar}^+$ ions. $\text{Ar}^+$ ions exhibit a steady state O/Ta ratio through the bulk oxide but $\text{Ar}_{1000}^+$ ions show a gradual decrease in the O/Ta ratio as a function of depth. The depth resolution and etch rate is substantially better for the monatomic beam compared to the cluster beam. Higher O concentrations are observed when the underlying Ta bulk metal is sputtered for the $\text{Ar}_{1000}^+$ profiles compared to the $\text{Ar}^+$ profiles.

1. Introduction

Tantalum pentoxide, $\text{Ta}_2\text{O}_5$, is technologically significant due to its dielectric properties [1] and applications in microelectronics [2] and optics [1, 3]. In addition, $\text{Ta}_2\text{O}_5$ grown on Ta foil is a well-established standard material for the determination of ion etch rate and depth resolution in compositional depth profiles obtained in electron spectroscopy [4]. Many authors use the
European standard (BCR-261T), which has a certified thickness of Ta$_2$O$_5$ grown on Ta foil as a reference to estimate the etch rate when performing XPS/AES depth profiles on other metal oxide thin films [5]. However, it is well known that monatomic argon (Ar$^+$) sputtering of Ta$_2$O$_5$ leads to the preferential sputtering of O [6] and this is generally considered to result from the difference in the atomic weight between Ta (180.95 u) and O (16.00 u) [7]. XPS studies of the preferential sputtering of oxygen from Ta$_2$O$_5$ have been performed by a number of workers [7-12]. Hofmann and Sanz performed the earliest in-depth study and they gave the steady-state TaO$_x$ stoichiometry (using 3 keV Ar$^+$) to be TaO$_{1.05}$ [7]. Holloway and Nelson sputtered Ta$_2$O$_5$ at varying incident Ar$^+$ energies between 0.5 and 5 keV and reported that greater preferential sputtering of O occurred at 0.5 keV than at higher energies and attributed this to the Ar$^+$ ions preferentially transferring their energy to O atoms [8].

It has been shown that there are a number of potential advantages in employing cluster beams (C$_{60}^+$, Bi$_n^+$, Au$_n^+$, Ar$_n^+$) in SIMS depth profiling of organic materials compared to monatomic sources, including reduced damage and roughening, lower penetration depth and higher sputter yield, enhancing the quality of chemical information obtainable, sputter rate and interface resolution [8, 9]. As a result, gas clusters are widely accepted as effective sources for the depth profiling of polymer samples without causing chemical damage or crosslinking [10]. Until recently, limited work had been published on the use of Ar$_n^+$ gas cluster ion beam (GCIB) sources for the XPS analysis and depth profiling of inorganic compounds, in particular metal oxides, despite their importance as functional thin films and corrosion resistant layers. As instruments with Ar$_n^+$ GCIBs are becoming more widespread, publications are now emerging in
the literature. Cumpson and co-workers have investigated $\text{Ar}_n^+$ GCIB analysis of HfO and ZnO [13,14] using Ar gas clusters of 1000 atoms ($\text{Ar}_{1000}^+$), corresponding to an average energy/atom ($E/n$) of 6 eV (the same conditions have also been employed in this work). They found that HfO exhibited no preferential sputtering of O using a 6 keV beam [13], whilst the work on ZnO was focused on optimising analytical conditions of inorganic interfaces and no information was given on the degradation (or not) of ZnO under these conditions [14]. Steinberger et al have examined FeO and Zn$_5$(CO$_3$)$_2$(OH)$_6$ (hydrozincite) using a range of different $\text{Ar}_n^+$ CGIB conditions [15]. Preferential sputtering of O was observed both for hydrozincite using $\text{Ar}_{2000}^+$ at incident energies of 4 keV ($E/n = 2$) and FeO using $\text{Ar}_{2000}^+$ at 6 keV ($E/n = 3$) [15]. Results of $\text{Ar}_n^+$ GCIB of single crystal SrTiO$_3$ have recently been reported by Aureau et al [16]. In that work, the $\text{Ar}_n^+$ GCIB experimental conditions are not entirely clear, but would appear to be $\text{Ar}_{3000}^+$ at an incident energy of 4 keV ($E/n = 1.33$). Under those conditions, the Ti 2p peak showed no evidence of reduced Ti states, but a small amount of reduction is observed in the Sr 3d peaks at longer etching times.

As a precursor to the more extensive work presented in this paper, we reported initial results on the $\text{Ar}_{1000}^+$ GCIB sputtering of the BCR-261T 30 nm Ta$_2$O$_5$ layer at incident energies of 4, 5 and 6 keV ($E/n = 4, 5$ and 6) [17]. That work showed the preferential sputtering of O for $E/n = 5$ and 6, but not at $E/n = 4$. At an $E/n = 4$, there was no evidence of sputtering occurring, whereas at $E/n = 5$ and 6, profiles through the 30 nm layer could be recorded. In some of the other work reported above, comparisons have been made between $\text{Ar}^+$ and $\text{Ar}_n^+$ GCIB sputtering [15-18]. In all cases, using optimized ion beam conditions, $\text{Ar}_n^+$ GCIB sputtering reduces the extent of damage observed compared to monatomic $\text{Ar}^+$ bombardment, offering the possibility of
performing XPS analysis and depth profiling of metal oxides with lower sputtering induced modification to the metal oxide and hence better quality data for the surface analyst.

The aim of this work is to employ the 30 nm thick Ta₂O₅ layer (BCR-261T standard) to: (i) investigate changes in chemical state associated with Ar⁺ and Arₙ⁺ bombardment; (ii) compare the preferential sputtering, etch rates observed and depth resolution for Ar⁺ and Arₙ⁺ depth profiles through the 30 nm thick Ta₂O₅ layer. Ar⁺ depth profiles were performed at ion beam energies of 500 eV and 3 keV and Ar₁₀₀₀⁺ depth profiles were acquired at ion beam energies of 6 keV and 8 keV (with and without sample rotation). The ion beam energies employed for the latter Ar₁₀₀₀⁺ depth profiles give rise to E/n values of 6 and 8 eV.

2. Experimental

The standard 30 nm Ta₂O₅ layer on Ta foil (BCR® -261T), described in [3] was employed for all XPS analyses undertaken. The XPS work was performed on a Thermo Scientific K-Alpha XPS system, equipped with the Ar⁺ and Arₙ⁺ gas cluster ion beam (GCIB) source, MAGCIS. The MAGCIS source is mounted at an angle of 60° to the sample normal. The ion beam area was rastered over an area of 1 mm² and to avoid crater edge effects, an X-ray spot diameter of 200 µm was employed. For monatomic Ar⁺ profiling, energies of 500 eV and 3 keV were employed, operating at beam currents of 1 and 3 µA (measured at the sample holder) respectively. For the Ar₁₀₀₀⁺ GCIB at 6 keV and 8 keV, a current of 20 nA was used. Ar₁₀₀₀⁺ GCIB profiles were also recorded at 6 keV and 8 keV using sample rotation at a rate of 1 rotation/min. The Ta₂O₅/Ta interface was assigned on the depth profiles using the linear drop in the O signal in the
interface region. The interface was taken as being the mid-point between the two positions on that O signal line (before and after the interface) where the signal deviates from linearity.

The XPS spectra were acquired employing a monochromated Al kα X-ray source operating at a power of 300 W. The spectrometer was calibrated using the Au 4f\textsubscript{7/2}, Ag 3d\textsubscript{5/2} and Cu 2p\textsubscript{3/2} peaks at 83.98, 368.26 and 932.67 and eV respectively. A pass energy of 50 eV and step size of 0.1 eV were employed. During ion beam bombardment, the X-ray source was blanked. Quantification was performed after a Shirley background subtraction and used Wagner sensitivity factors, modified to account for the instrument transmission function. The Thermo Scientific Avantage software was employed for peak fitting, using a Gauss/Lorentz mix value of 26%.

As the Ar\textsubscript{n}\textsuperscript{+} cluster etch rates were much lower than the Ar\textsuperscript{+} etch rates, the XPS data recorded at each level of the GCIB depth profile was performed using the “snapshot analysis” mode. In this mode, the pass energy of the analyser is increased from 50 eV to 150 eV and rather than scanning through the selected energy range, the electron signal from the entire range is recorded simultaneously. This sacrifices some of the energy resolution but greatly reduces the acquisition time. The spectral resolution is then mostly recovered using a deconvolution process during data analysis, see Figure 1.
Figure 1: XPS spectra of the Ta 4f spectrum acquired; (a) in ‘snapshot analysis’ mode; (b) in ‘snapshot analysis’ mode after deconvolution to simulate a pass energy of 50 eV; (c) a Ta 4f spectrum acquired with a pass energy of 50 eV.

To ensure accurate peak fitting, a 3 keV Ar\(^+\) depth profile was initially peak fitted to establish the peak fitting parameters with which all subsequent depth profiles were fitted.

3. Experimental results

3.1. XPS spectra and depth profiles

In order to establish the Ta chemical states observed during depth profiling of the Ta\(_2\)O\(_5\) layer, a methodical approach was adopted in fitting the Ta 4f spectra, using the known binding energies for the metallic tantalum doublet and well reported peak positions of the Ta\(_2\)O\(_5\) doublet. These two pairs of peaks represent spectra at the beginning and the end of the depth profile, thus could be easily isolated and accurately fitted.

Figure 2: XPS Ta 4f peaks: (a) prior to depth profiling, with the Ta\(^{5+}\) 4f\(_{7/2}\) and 4f\(_{5/2}\) peaks fitted; (b) after depth profiling the metallic Ta\(^0\) 4f\(_{7/2}\) and 4f\(_{5/2}\) peaks fitted.
Both pairs of peaks shown in figure 2 are important for peak fitting Ta depth profiles. The metallic peaks, $\text{Ta}^0$ represent the surface composition once the 30 nm oxide layer has been removed from the $\text{Ta}_2\text{O}_5$ foil. Ensuring that these peaks appear at the correct binding energies is important as their position influences the positions of the other peaks in the spectra. As $\text{Ta}^0$ is electrically conductive, both peaks in the doublet show the high binding energy tail associated with shake-up events for electrons close to the Fermi level, yielding an asymmetric peak shape that is unlike the other Ta oxide components fitted in the depth profile. This peak shape was taken into account when fitting the $\text{Ta}^0$ peaks.

The initial $\text{Ta}^{5+}$ peaks must be fitted correctly as they provide the peak shape for the subsequent sub-oxide peaks that are produced by preferential etching of O from $\text{Ta}_2\text{O}_5$. Once fitted, the $\text{Ta}^{5+}$ peaks were used to set the FWHM, the L/G mix ratio as well as the relative intensity and separation ratios between the Ta 4f$_{7/2}$ and Ta 4f$_{5/2}$ peaks for each sub-oxide state.

In fitting the final Ta peak envelope, all of these variables were fixed for each of the sub-oxide states to ensure that the only variation between them were the binding energies and peak intensities. However, the FWHM of the peaks fitted to the spectra after ion bombardment were allowed to increase to accommodate ion beam induced broadening.

For the $\text{Ta}_2\text{O}_5$ profile, in addition to $\text{Ta}^0$ and $\text{Ta}^{5+}$, the other possible sub-oxide reduction states that can be generated during ion etching are $\text{Ta}^{4+}$, $\text{Ta}^{3+}$, $\text{Ta}^{2+}$, and $\text{Ta}^{1+}$, representing $\text{TaO}_2$, $\text{Ta}_2\text{O}_3$, TaO and $\text{Ta}_2\text{O}$ respectively. Obtaining a good and reliable fit for the Ta 4f envelope at various stages of the profile required all four of the possible sub-oxide doublets. The binding energies...
of the sub-oxide peaks were based upon values found in the literature and the values taken from an approximate depth of 20 nm into the oxide layer are given in Table 1. [11-12]. Figure 3 shows that there is a linear progression of the binding energy with oxidation state, as found by Benito and Palacio for Ta$_2$O$_5$ under ion bombardment and the peak binding energies for the different Ta oxidation states are all within ± 0.4 eV of their reported values [12].

Table 1: XPS Ta 4f binding energies and FWHM employed in the peak fits for the Ta$_2$O$_5$ depth profiles.

| Sub-Oxide State | Binding energy (eV) | FWHM (eV) |
|-----------------|---------------------|-----------|
|                 | Ta4f 7/2            | Ta4f 5/2  | Ta4f 7/2 | Ta4f 5/2 |
| Ta$^0$ (metal)  | 21.50               | 23.42     | 0.73     | 0.73     |
| Ta$^{1+}$ (Ta$_2$O) | 22.5 ± 0.10         | 24.4 ± 0.10 | 1.45     | 1.45     |
| Ta$^{2+}$ (TaO) | 23.3 ± 0.30         | 25.2 ± 0.30 | 1.45     | 1.45     |
| Ta$^{3+}$ (Ta$_2$O$_3$) | 24.3 ± 0.20       | 26.2 ± 0.20 | 1.45     | 1.45     |
| Ta$^{4+}$ (TaO$_2$) | 25.7 ± 0.30         | 27.6 ± 0.30 | 1.45     | 1.45     |
| Ta$^{5+}$ (Ta$_2$O$_5$) | 27.0 ± 0.05         | 28.9 ± 0.05 | 1.45     | 1.45     |
Figure 3: A plot showing the linear progression the Ta 4f$_{7/2}$ binding energies with increasing Ta$^{n+}$ oxide state.

The peak positions as shown in Table 1 are constrained throughout the depth profiles with a maximum variation of $\pm$ 0.03 eV. The FWHM of the Ta$^5+$ 4f doublet components for the native Ta$_2$O$_5$ spectra was 1.23 eV and the FWHM of the Ta$^0$ 4f doublet components after sputtering spectra was 0.76 eV. The FWHM for the Ta 4f doublet components for all oxide Ta$^{n+}$ states after Ar$^+$ and Ar$_{1000}^+$ bombardment broadened to 1.45 eV (Table 1).
Figure 4: XPS Ta 4f peak taken from a depth of approximately 20 nm into a 30 nm Ta$_2$O$_5$ foil, fitted with Ta$^{5+}$, Ta$^{4+}$, Ta$^{3+}$, Ta$^{2+}$, Ta$^{1+}$ and Ta$^0$ components. The Ta 4f peak is taken from profiles recorded with the following ion beam conditions: (a) 3 keV Ar$^+$; (b) 500 eV Ar$^+$; (c) 6 keV Ar$_{1000}^+$. 

Figure 5: XPS depth profiles of 30 nm Ta$_2$O$_5$ foil etched using; (a) 3 keV Ar$^+$; (b) 500 eV Ar$^+$. Carbon has been included in the 3 keV Ar$^+$ profile, but excluded from the 500 eV Ar$^+$ profile.
Spectra taken from the 3 keV and 500 eV Ar\textsuperscript{+} profiles and the 6 keV Ar\textsubscript{1000}\textsuperscript{+} profile are shown in Figure 4 and depth profiles for Ar\textsuperscript{+} ion bombardment at 3 keV and 500 eV are presented in Figure 5. The surface carbon contamination has been included in the profile and the results show that this layer is removed after about 3 nm of material has been sputtered away. As the carbon contamination layer was not of interest in this work, the C 1s data has been excluded from subsequent depth profiles shown in Figure 5 (b) and later figures. The relative etch rates were 4.8 x 10\textsuperscript{-3} and 2.7 x 10\textsuperscript{-3} nm/min at 3 keV and 500 eV respectively. The steady state composition was determined to be TaO\textsubscript{1.55} and TaO\textsubscript{1.50} at incident energies of 3 keV and 500 eV respectively. This represents a reduction in the preferential sputtering of O compared to the results of Hofmann and Sanz, who found a steady state composition of TaO\textsubscript{1.05} at 3 keV [7]. However, there are differences in the ion beam current density and incident angle of ion bombardment between the two studies. The greater preferential sputtering of O at lower incident ion beam energies is in agreement with the results of Holloway and Nelson [8]. The depth resolution, Δz, of the interface region (uncorrected for escape depth influence) was calculated from the depth profiles as etch depth corresponding to the O 1s signal dropping from 84 to 16% of its maximum signal, where the maximum is taken from the steady-state region of the profile. The depth resolution determined for the 3 keV and 500 eV monatomic depth profiles were very similar, being 3.8 and 4.0 nm respectively.

A similar depth profile for the Ar\textsubscript{1000}\textsuperscript{+} GCIB at 6 keV is presented in figure 6 (a). There are three points to note: (i) the absence of a steady state region, where the composition of the altered layer is constant; (ii) once the Ta\textsubscript{2}O\textsubscript{5} layer has been removed, the O concentration drops to a steady state value of around 10 at.% rather than a much lower value, as seen for the
monatomic Ar\(^+\) depth profiles; (iii) the depth resolution is substantially degraded compared to the monatomic Ar\(^+\) profiles. With regard to all of these effects, profiles using the same ion beam conditions were repeated a number of times and the same trends were observed in all cases. Introducing sample rotation during profiling and performing the Ar\(_{1000}\)^+ GCIB profiles at 6 keV and 8 keV resulted in the profiles shown in Figure 6 (b) and (c) respectively.

Interestingly, sample rotation fails to influence the high concentration of O seen once the Ta oxide layer has nominally been removed. This would suggest that sample roughness is not the cause of this high residual O concentration. The O 1s peak was always the first peak to be recorded when the ‘snapshot analysis’ mode was employed. This analysis procedure would be expected to minimise re-oxidation of the surface during analysis.

Sample rotation and an increase in beam energy to 8 keV appears to accentuate the decline in the O concentration with depth whilst profiling through the Ta\(_2\)O\(_5\) layer and at no point is there a progressive linear decrease in the O concentration with depth, as seen for the 6 keV Ar\(_{1000}\)^+ GCIB profile without sample rotation.
For the 6 keV cluster ion depth profile without sample rotation, taking the inflection point where the linear decline in the O concentration first changes to a more rapid non-linear decline and using the same methodology as described previously, the depth resolution has increased to 11 nm, compared to the ≈4 nm observed for the monatomic ion profiles. Concerning the degree of preferential sputtering of O for the 6 keV Ar\textsubscript{1000}\textsuperscript{+} GCIB profile compared to the monatomic Ar\textsuperscript{+} profiles, taking the elemental concentrations at a depth of 10 nm (a point approximately in the middle of the linear region of the profile) the metal oxide stoichiometry is TaO\textsubscript{2.0}, thus there is less preferential sputtering of O compared to the monatomic Ar\textsuperscript{+} sputtering. This is in

Figure 6: XPS depth profiles of 30 nm Ta\textsubscript{2}O\textsubscript{5} foil etched using: (a) 6 keV Ar\textsubscript{1000}\textsuperscript{+}; (b) 6 keV Ar\textsubscript{1000}\textsuperscript{+} including sample rotation; (c) 8 keV Ar\textsubscript{1000}\textsuperscript{+} including sample rotation
agreement with the other studies comparing $\text{Ar}_n^+$ and $\text{Ar}^+$ sputtering of metal oxide based materials [15-18].

To provide more information on the change in $\text{Ta}^{n+}$ chemical states during the $\text{Ta}_2\text{O}_5$ depth profiles, $\text{Ta} 4f$ spectra for monatomic $\text{Ar}^+$ sputtering at 3 keV and 500 eV and $\text{Ar}_{1000}^+$ GCIB at 6 keV (not rotated) are given in Figure 7.

![Figure 7](Image)

Figure 7: Progression of the $\text{Ta} 4f$ spectra during depth profiling of a 30 nm $\text{Ta}_2\text{O}_5$ foil for: (a) 3 keV $\text{Ar}^+$; (b) 500 eV $\text{Ar}^+$; (c) 6 keV $\text{Ar}_{1000}^+$. 

To make a direct comparison of $\text{Ta} 4f$ peakshape changes over the “steady state” region for the depth profiles recorded using 3 keV $\text{Ar}^+$ and 6 keV $\text{Ar}_{1000}^+$, it is also useful to plot overlays of the spectra $\text{Ta} 4f$ spectra, as shown in Figure 8. The difference between the $\text{Ar}^+$ and $\text{Ar}_{1000}^+$ is clear, with the variation in $\text{Ta} 4f$ envelope for 3 keV $\text{Ar}^+$ being minimal, whilst for the 6 keV $\text{Ar}_{1000}^+$, the peakshape progressively changes with depth.
Figure 8: Overlay of Ta 4f spectra recorded from the Ta bulk oxide region of the 30 nm Ta$_2$O$_5$ foil using ion beam conditions of: (a) 3 keV Ar$^+$ (corresponding to the ‘steady state’ region); 6 keV Ar$_{1000}$ (corresponding to the ‘steady state equivalent’ region where the O concentration shows a gradual linear decline).

Comparing the Ta 4f peak envelope in the ‘steady state’ region for the monatomic and cluster ion beam depth profiles, in all cases there are 4 main peaks/shoulders at around 29 eV, 27.5 eV, 24.0 eV and 22.5 eV. The intensity of the peaks at 29 and 27 eV progressively decrease in intensity and the peaks at 24.0 eV and 22.5 eV progressively increase in intensity as a function of depth for the 6 keV Ar$_{1000}$ profile. To investigate this in a more quantitative manner, the intensity of each oxide state throughout the depth profiles was plotted and these profiles are shown in Figure 9.
Comparing these depth profiles reveals some interesting information about the existence and depth variation of sub-oxide states in the altered layer for the different etching conditions. However, due to the complexity of fitting the Ta 4f peak envelope, it is important to be mindful that the peak fitting may not be entirely accurate and truly representative of the behaviour of each oxidation state as a function of depth. Consequently, over interpretation of the data should be avoided. Nevertheless, some important trends can be extracted from the data and it is reasonable to separate the sub-oxide states into 2 groups, (Ta^{4+} and Ta^{5+}) representing the higher oxidation states and (Ta^{2+} and Ta^{+}) representing the lower oxidation states. A comparison between the Ar^{+} and Ar_{1000}^{+} depth profiles in Figure 9 reveals that when profiling through the bulk oxide, Ar^{+} bombardment gives rise to a clear preference in the formation of the lower Ta^{n+} oxidation states in the altered layer rather than the higher oxidation states. In
contrast, \( \text{Ar}_{1000}^+ \) bombardment results in a greater concentration of higher oxidation states compared to the lower oxidation states. Furthermore, as expected, for the monatomic \( \text{Ar}^+ \) profiles, it can be seen that over the steady state region, the intensities of each of the \( \text{Ta}^{n+} \) states remain constant. However, for the 6 keV \( \text{Ar}_{1000}^+ \) profile, this is not the case, with a gradual decline in the intensity of the higher oxidation states and concomitant gradual increase in the intensity of the low oxidation states as a function of depth. This effect is even more pronounced in the depth profiles for the \( \text{Ar}_{1000} \) GCIB at 6 keV and 8 keV including sample rotation where again the behaviour for each oxidation state is plotted as a function of depth (Figure 10).

![Figure 10](image)

**Figure 10:** XPS depth profiles of 30 nm \( \text{Ta}_2\text{O}_5 \) on Ta foil showing the progression of the different \( \text{Ta}^{n+} \) states when etched using: (a) 6 keV \( \text{Ar}_{1000}^+ \) including sample rotation; (b) 8 keV \( \text{Ar}_{1000}^+ \) including sample rotation.

For these \( \text{Ar}_{1000}^+ \) cluster beam profiles including sample rotation, there is a clear enhancement in the formation of the higher oxidation states in the altered layer during removal of the initial 10-15 nm of oxide. In this region, the lower oxidation states are formed, but at lower concentrations. The concentration of the higher oxidation states in the altered layer peaks at a depth between 5 and 10 nm and then slowly declines until the \( \text{Ta}^0 \) concentration stabilises at
greater depths. On the other hand, the lower oxidation states show a gradual increase in concentration within the altered layer as a function of depth into the oxide layer. The variation in concentrations of the sub-oxide states and trends of lower levels of high oxidation states (and higher levels of lower oxidation states) with increasing depth are consistent with the absence of a steady state region and progressive decline in the O concentration observed for the depth profile through the Ta$_2$O$_5$ layer for the Ar$_{1000}^+$ beam profiles. As a result of this, unlike the behaviour for the Ar$^+$ profiles, for the Ar$_{1000}^+$ GCIB profiles, the levels of the sub-oxide states are constantly changing with depth.

3.2. Etch rate

Use of the 30 nm thick BCR®-261T standard enables the etch rate to be accurately determined for all of the Ar$^+$ ions and Ar$_{1000}^+$ ion depth profiles performed. A comparison of the etch rates for the different ion beam conditions, given in Table 2, is of particular interest to the practical analyst. The etch rates for the monatomic Ar$^+$ beam (at 3 keV and 500 eV) are approximately 2 orders of magnitude higher than for Ar$_{1000}^+$ GCIB at 6 keV (rotated and un-rotated) and 1 order of magnitude higher than for Ar$_{1000}^+$ GCIB at 8 keV (rotated). Rotating the sample for the Ar$_{1000}^+$ GCIB at 6 keV leads to an increase in the etch rate by approximately 4 times.
Table 2: Etch rates for different Ar\(^+\) and Ar\(_n^+\) beam conditions when sputtering through the 30 nm thick Ta\(_2\)O\(_5\) layer on Ta.

| Ion beam conditions | E/n (eV) | Time to Interface (s) | Etch Rate (nm/min) |
|---------------------|----------|-----------------------|--------------------|
| 6 keV Ar\(_{1000}^+\) | 6        | 26158 (7 hrs)         | 1.8 x10\(^{-5}\) |
| 6 keV Ar\(_{1000}^+\) (Rotated) | 6 | 7344 (122 mins) | 6.8 x10\(^{-5}\) |
| 8 keV Ar\(_{1000}^+\) (Rotated) | 8 | 1287 (21 mins) | 3.8 x10\(^{-4}\) |
| 500 eV Ar\(^+\) | 500      | 185                   | 2.7 x10\(^{-3}\) |
| 3 keV Ar\(^+\) | 3000     | 103                   | 4.8 x10\(^{-3}\) |

Taking account of the different ion current densities employed in the different studies, the etch rates for the Ar\(_{1000}^+\) GCIB at 6 keV in this work are consistent with our previous values of 1 x 10\(^{-3}\) nm/s for the same BCR -261T standard recorded on a Thermo Scientific ThetaProbe instrument [17] and similar to the etch rate of 4.2 x 10\(^{-4}\) nm/s for HfO reported by Barlow et al [13] recorded on a Thermo Scientific ThetaProbe instrument equipped with the same MAGCIS source as used in this work.

4. Discussion

This work is the first reported example of an XPS depth profile through an inorganic layer using an Ar\(_n^+\) GCIB. The results have shown that despite the much lower E/n, Ar\(_n^+\) GCIB bombardment using Ar\(_{1000}^+\) GCIB at 6 keV and 8 keV still leads to the preferential sputtering of O for Ta\(_2\)O\(_5\).
However, the extent of preferential sputtering is lower than that observed using a monatomic Ar\(^+\) beam at 3 keV or 500 eV. The Ar\(_{1000}^+\) profiles have shown some rather surprising results:

(i) the depth resolution is substantially degraded compared to the monatomic Ar\(^+\) profiles

(ii) the absence of a steady state region in the oxide, where the composition of the altered layer is constant. Instead, the O concentration gradually decreases as the profile progresses towards the interface

(iii) once the Ta\(_2\)O\(_5\) layer has been removed, the O concentration drops to a value of 10 – 20 at.% rather than a much lower value, as seen for the monatomic Ar\(^+\) depth profiles.

With regard to the penetration depth of the ion beams, using molecular dynamic simulations, Aoki et al [19] reported that the penetration depth of Ar\(_{688}^+\) clusters dropped to below 5 Å when the average E/n was 14 eV. The average E/n of the Ar\(_{1000}^+\) used in this study were lower than this value, being 8 and 6 eV, thus penetrating just 1 - 2 monolayers into the sample surface. In contrast, the penetration depths for monatomic Ar\(^+\) at 3 keV and 500 eV calculated using SRIM calculations [20] is 3.5 nm and 1.3 nm respectively. However, using the experimental set-up described here yields the unexpected result that the lower penetration depth does not lead to improved depth resolution when profiling the Ta\(_2\)O\(_5\) layer on Ta; instead the depth resolution is degraded. For the profiles recorded using Ar\(_{1000}^+\) clusters at 8 keV and 6 keV with rotation compared to that recorded for Ar\(_{1000}^+\) clusters at 6 keV without rotation the depth resolution is further worsened. Surface roughening and nano-topography resulting from Ar\(^+\) bombardment are well-known phenomena which are influenced by many experimental parameters, including the ion beam incident angle, energy, flux and fluence [21]. Simulations of Ar clusters of various sizes and energies with the incident beam inclined at an angle of 60\(^\circ\) with
respect to the surface normal bombarding different material surfaces have shown the formation of ripple and dot structures (but the extent of the roughening was not stated) [22]. However, considering the known low penetration depth of the Ar clusters, sample rotation causing further interface broadening (when it would be expected to reduce roughening) and the large degree of interface broadening observed for a 30 nm thick film, it seems unlikely that roughening is the main cause of the interface broadening observed for the Ar\textsubscript{1000}\textsuperscript{+} depth profiles reported here for Ta\textsubscript{2}O\textsubscript{5}.

It has been reported that the impact of cluster ions with solids leads to high temperature and pressure transients in the vicinity of the impact which do not occur in an equivalent manner for Ar\textsuperscript{+} bombardment [22-25]. An increase in surface temperature for samples being bombarded with an argon cluster beam can lead to various effects including an increase in sputtering yield and changes in the interface width [26, 27]. Infusion doping of elements into solids through the use of dopants in Ar clusters has been described [28] and in the recently published book by Yamada, it is stated that the intense Ar cluster thermal spike allows the infusion of elements into the solid surface by an atomic mixing process which occurs within the thermal transient region [29].

Preferential sputtering of O from metal oxides can be caused by a number of different processes, where in many cases it is thought that a combination of mechanisms may be influencing the altered layer composition [30, 31]. The preferential sputtering of O from Ta\textsubscript{2}O\textsubscript{5} is generally considered to be a ballistic process [7,30]. From the discussion above, there are a number of differences between the incident Ar\textsubscript{1000}\textsuperscript{+} and Ar\textsuperscript{+} ion beams and their consequent physical/chemical effects which could be leading to the variations seen in the Ar\textsubscript{1000}\textsuperscript{+} and Ar\textsuperscript{+}
profiles. For 6 and 8 keV $\text{Ar}_{1000}^+$ bombardment, there is a much lower $E/n$, reduced penetration depth and more intense temperature and pressure transient compared to 0.5 and 3 keV $\text{Ar}^+$ bombardment. Any one, or a combination of these experimental parameters/effects, could be exerting the strongest influence over the observed reduced preferential sputtering of O, progressive O loss, interface broadening and higher O concentrations present in the underlying Ta metal for the $\text{Ar}_{1000}^+$ compared to the $\text{Ar}^+$ profiles. Thus, the exact mechanisms are not known. However, it is possible the higher thermal transient in the surface region associated with the 6 and 8 keV $\text{Ar}_{1000}^+$ may be the cause of the observed progressive O loss for the cluster profiles. Many metal oxides are known to thermally decompose when heated in vacuum environments and the thermal reduction of $\text{Ta}_2\text{O}_5$ in vacuum has been reported [32]. Thus, the observed progressive O loss from the surface for the 6 keV $\text{Ar}_{1000}^+$ profile (without rotation) may be due to a combination of ballistic based preferential sputtering and oxide reduction, with the latter effect being cumulative as a function of sputter time. If this hypothesis is correct, then the decrease in the O/Ta ratio for the $\text{Ar}_{1000}^+$ profile with sample rotation compared to that without sample rotation would suggest that there is a greater rise in temperature for the former case, which increases the sputter yield through a lowering of the surface binding energy [26], consistent with the observed increase in the etch rate. The interface broadening effect, rather than being caused by roughening, is more probably due to a thermodynamically driven and thermally induced diffusion process across the interface with the higher extent of interface broadening observed for the 6 keV (with rotation) and 8 keV $\text{Ar}_{1000}^+$ profiles being caused by more intense thermal spikes. The same process could be responsible for the high O concentrations observed when initially profiling into the underlying Ta metal.
From the viewpoint of the practical analyst, for the Ar\textsubscript{1000}\textsuperscript{+} cluster profiles, the absence of a steady-state O concentration in the oxide, degraded depth resolution and high O concentrations observed in the substrate are clearly problematic. Further research work is required to find experimental conditions which minimise or eradicate these detrimental effects and improve the quality of the XPS depth profile.

The results presented here represent early work on the GCIB Ar cluster profiling through metal oxide layers. The Ta\textsubscript{2}O\textsubscript{5} on Ta layers studied may present particularly difficult analytical issues compared to other metal oxides and other inorganic materials. For example, no preferential sputtering of oxygen was observed for HfO under 6 keV Ar\textsubscript{1000}\textsuperscript{+} bombardment [13] and similar to the results of Aureau et al [16], recent results have shown for a SrTiO\textsubscript{3} thin film on Si that the 8 keV, Ar\textsubscript{300}\textsuperscript{+} depth profile is very comparable to the 500 eV Ar\textsuperscript{+} profile, with no preferential sputtering of O in either case, similar interface broadening and a better retention of the SrTiO\textsubscript{3} stoichiometry for 8 keV, Ar\textsubscript{300}\textsuperscript{+} [33]. For Ar\textsubscript{n}\textsuperscript{+} cluster depth profiles, in a similar manner to Ar\textsuperscript{+} profiles of different inorganic materials, there are likely to be various different ion beam induced processes which introduce artefacts into the profiles and the susceptibility to these effects is material dependent. However, with Ar cluster depth profiling, there is a large GCIB parameter space to be explored which has the potential to offer greater possibilities for minimising such undesirable effects.

5. Conclusions
Depth profiles through the certified (European standard BCR-261T) 30 nm thick Ta₂O₅ layer grown on Ta foil using monatomic Ar⁺ and Ar₁₀₀₀⁺ cluster ions have been performed using a GCIB at different incident energies. The preferential sputtering of O, relative intensities of Ta oxidation states, depth resolution and etch rates obtained from the profiles using the different ion beam conditions have been recorded and compared. The following conclusions can be drawn from this investigation:

The preferential sputtering of O induced using 6 keV Ar₁₀₀₀⁺ ions is lower relative to 3 keV and 500 eV Ar⁺ ions. At a point close to the middle of the 30 nm thick oxide, the stoichiometry recorded for the 6 keV Ar₁₀₀₀⁺ ion beam was TaO₂.₀, compared to TaO₁.₅ and TaO₁.₅₅ for Ar⁺ at 3 keV and 500 eV respectively.

Depth profiles recorded using Ar⁺ ions give rise to a steady state region in the oxide bulk, where the preferential sputtering of O remains constant. The use of 6 keV Ar₁₀₀₀⁺ ions shows a gradual decrease in the O concentration over the same region. This progressive loss of O as a function of depth is further enhanced when the experimental conditions are changed through the use of sample rotation and an increase in the Ar₁₀₀₀⁺ incident energy to 8 keV. Curve fitting has shown that the concentration of the higher Ta oxidation states (Ta⁴⁺ and Ta⁵⁺) is greater than the lower oxidation states (Ta⁺ and Ta²⁺) in the Ar⁺ profiles and the opposite trend is observed for the Ar₁₀₀₀⁺ profiles. Furthermore, for the Ar₁₀₀₀⁺ profiles, there is an increased concentration of the higher oxidation states closer to the surface and the concentration of lower oxidation states progressively increases with depth.
The Ar\(^+\) depth profiles recorded using ion beam energies of 500 eV and 3 keV (without sample rotation) exhibit a better depth resolution than Ar\(_{1000}\)\(^+\) profiles at beam energies of 6 keV and 8 keV (with and without sample rotation).

There is a higher O concentration observed when profiling into the underlying Ta for profiles performed using 6 keV and 8 keV Ar\(_{1000}\)\(^+\) which is not observed for the 3 keV and 500 eV Ar\(^+\) profiles.

The etch rate increases with E/n. Using a 3 keV Ar\(^+\) beam, the etch rate was found to be 4.8 x 10\(^{-3}\) nm/min. For the 6 keV Ar\(_{1000}\)\(^+\) beam, the etch rate decreased to 1.8 x 10\(^{-5}\) nm/min. Increasing the Ar\(_{1000}\)\(^+\) ion beam energy to 8 keV and rotating the sample during profiling leads to a significant increase in the cluster beam etch rate (3.8 x 10\(^{-4}\) nm/min).

It is proposed that for the Ar\(_{1000}\)\(^+\) depth profiles, the progressive O loss from the oxide and increased interface width may be caused by the high temperature transient resulting from the cluster impact.

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