In this study, we demonstrate low damage etching of titania for depth profile analysis using large Ar cluster ions. Sample damage caused by impinging ion beams is discussed and a comparison is made between monatomic Ar$^+$ ions and Arn$^+$ cluster ions with respect to surface damage. Monatomic ions of beam energy 5 kV cause considerable changes to the structure of amorphous titania resulting in the preferential removal of oxygen and damage to the lattice structure. Titanium is reduced from the +4 oxidation state to +3 and +2 oxidation state during this preferential removal. In contrast, the use of clusters greatly diminishes this damage and also reduces the incorporation of the impinging ion into the sample surface. Here we discuss the use of Arn$^+$ clusters as a new methodology for reducing the damaging effects caused by ion bombardment.

1. Overview

Depth profiles have been employed extensively to accurately gain information regarding elemental concentration and chemical composition of complex heterogeneous materials. The process involves repetitive cycles of analysis – in this case employing XPS as the analytical technique – followed by ion bombardment. Ion bombardment removes the top layers each time, exposing bulk material. The difference in the chemical composition of the surface relative to the sub-surface or bulk is often significant to the mechanical or electrical performance of the material. Until the recent development of Arn$^+$ gas cluster ion sources such depth profile studies have been limited to Ar$^+$ as the primary ion for sputter erosion however we show that by using cluster ions, where the energy per atom can be as low as 5-40 eV, it is possible to significantly reduce bulk damage and preferential sputtering of these complex surfaces.

Here we will discuss the use of clusters for depth profiling a titania thin-film. Titania is used in a wide variety of applications from solar cells to heterogeneous catalyst supports. Its many uses can be attributed to its formidable electron transport properties. Unfortunately analysis using depth profile methods has until now been limited due to its readiness to reduce under ion bombardment. Here we will introduce a new methodology which limits this damaging process.

2. Experimental

All measurements were taken using the Kratos Axis Nova XPS instrument equipped with a Kratos Gas Cluster Ion Source (GCIS) for sample sputtering using Arn$^+$ cluster ions or monatomic Ar$^+$. Clusters are created in the GCIS through the supersonic expansion of high pressure Ar gas through a de Laval nozzle into a medium vacuum region [1]. Nascent clusters are transmitted through a differentially pumped region into an electron impact ionisation source. Following ionisation, Arn$^+$ cluster ions are extracted through the length of a Wien filter to eliminate all small ions and limit the transmitted cluster size distribution spread around a chosen median value. The Arn$^+$ cluster ions are then deflected through 2°
to eliminate neutral and metastable species from the beam before simultaneous focusing and rastering across the sample. Alternately, Ar gas can be directly introduced into the electron impact ionisation source to allow production of monoatomic Ar$^+$ ions.

The GCIS can deliver Ar$_n^+$ cluster ions at energies from 1–20 keV and cluster sizes $n = 250$–2000 so it is worthwhile to carefully select the beam parameters most suited to the application. Most published data using Ar$_n^+$ cluster ion sputtering has concerned the etching of organic material where relatively high sputter yields allow the practical use of low beam energies for high resolution depth profiling [2,3]. Recent data published by Cumpson et al. [4,5] illustrates the necessity of using Ar$_n^+$ cluster ions of relatively higher energy per nucleon to achieve practically useful sputtering yields when etching the types of inorganic materials of interest here. Considering the semi-empirical relationship [3,4]:

$$Y(\varepsilon) = n eA \left( 1 + erf \left( \frac{\varepsilon - U}{s} \right) \right)$$  \hspace{1cm} (1)

where $Y$, $\varepsilon$, $A$ and $s$ represent sputtering yield, cluster energy per nucleon, a constant and the energy range of atoms within the cluster upon impact, respectively. The crucial parameter here is $U$, the effective atomic sputtering threshold. Values of $U$ for organic materials typically $\approx 2$ eV, whereas values for inorganic and metallic materials (e.g. SiO$_2$, Au, TiO$_2$) have been found to be an order of magnitude larger $\approx 20$ eV [3,4]. In simple terms, the Ar$_n^+$ cluster ion energy per nucleon, $\varepsilon$, must exceed this effective threshold for sputtering to occur. Consequently, Ar$_n^+$ cluster ion beams of 20 keV $n = 500$ ($\varepsilon \sim 40$ eV nucleon$^{-1}$) with a 1.25 mm $\times$ 1.25 mm raster area are employed in this study unless stated otherwise. It is also useful to consider the work on Ar$_n^+$ cluster ion sputter yield relationships of a range of materials by Seah [5]. By inspection of Fig. 11 of Reference [5] the resulting value of $\varepsilon \sim 40$ eV nucleon$^{-1}$ should deliver a similar sputtering yield for an organic material using an Ar$_n^+$ cluster ion beam with only $\varepsilon \sim 3$ eV nucleon$^{-1}$. For irradiation of samples with monoatomic Ar$^+$, a beam energy of 5 keV is used throughout to be consistent with standard practice. The ion incidence angle was 50° to the sample surface. The detection angle was normal to sample surface. The sample current for the monatomic ions was $\sim 4$ $\mu$A and for the Argon clusters $\sim 30$ nA.

Titania thin-films were prepared via spray-pyrolysis on FTO glass. The films were annealed at 450 C and were shown by XRD to be an amorphous mix or both the rutile and anatase states.

3. Results and Discussion

For comparison, a depth profile experiment of the titania thin-film was first performed using 5 kV monoatomic Ar$^+$ ions. After each etch a XP spectrum was acquired for the Ti 2p region to monitor the chemical changes taking place. As expected, a drastic change in the peak position of Ti 2p$_{3/2}$ was observed. Figure 1 shows the change in structure of the Ti 2p peak after sputtering the film to a depth of 20 nm.

This change in peak shape has previously been attributed to a reduction in the oxidation state of the material [6]. In order to characterize this damage, the degree in reduction of titanium is needed and the spectra need to be fitted accordingly. A variety of peak positions have been attributed to the different oxidation states of reduced titanium oxides and there is inconsistency in the literature as to the actual values of the binding energy shift of the Ti 2p$_{3/2}$ from +4 to +3 and +2 oxidation states. For +3 a shift range of $-1.5$ to $-2.5$ has been reported [7,8]. For +2 a shift range of $-2.5$ to $-3.9$ have also been reported [7,9]. Using these ranges it was possible to accurately peak-fit the sputtered spectrum by carefully
constraining the fitting limits and algorithm. We have no 
a priori reason to believe that these fitting functions
represent the “true” chemical shifts and peak shapes,
however the constraint of these parameters leads to
results that are at least systematic and can be used to
illustrate trends. Figure 2 shows the sputtered spectra
fitted with peaks attributed to titanium in the +4 (458.9
eV), +3 (457.3 eV) and +2 (455.7 eV) oxidation states.
Interestingly metallic Ti — which has a well character-
ized shift of −5.2 from the position of TiO$_2$ — was not
observed indicating that titanium does not behave like
similar transition metals which oxides can be sputter
reduced back to their metallic oxidation state.

Having illustrated the damage caused by monatomic
Ar$^+$ ions, 20 kV Ar clusters of $n = 500$ were used for
comparison. Figure 3 shows the XP spectra for the Ti 2p
region of the thin-film sputtered 20 nm deep. As with
monatomic ions, there is a decrease in the intensity of the
+4 oxidation state peak and an increase in the lower
binding energy shoulder attributed to the +3 oxidation
state. There is however very little further reduction to the
+2 oxidation state. In Fig. 4 a comparison is made
between the Ti 2p spectra for both sputter modes.

The distinct differences can be attributed to the
different sputtering mechanism of cluster ions. Unlike
monatomic argon, the low partition energy per Argon
atom in the cluster ions means that the penetration depth
is restricted to the near surface region. We estimate the
penetration depth of the cluster ions to be ~6 nm, which
is shallower than the analysis depth of XPS. A shallow
impact crater is created upon each collision and little
damage is projected into the bulk structure. The high
energy density and efficient lateral sputtering mechanism
is responsible for the high ion yield and etch rate of >4
nm/min. This mechanism removes most of the damaged
surface material which enters the vacuum leaving
minimal damage but more importantly a pristine material

![Fig. 2](image2.png)

**Fig. 2** Peak-fitted Ti 2p region after the thin-film was etched.

![Fig. 3](image3.png)

**Fig. 3** Ti 2p spectrum when sputtered 20 nm deep using 20 kV Ar$^{500+}$.

![Fig. 4](image4.png)

**Fig. 4** A comparison of the change in Ti 2p spectrum when sputtered 20 nm using different ion sources.
within the sampling depth of XPS. An important consideration when performing and depth profile experiment is the etch rate for the sample. The Argon atoms in an Ar\textsubscript{500}\textsuperscript{+} ion with energy 20 kV have an average energy of 40 eV. If a similar energy were used with monatomic Argon ions the etch rates would be so low as to be impractical for almost all applications.

Another important consideration when depth profiling inorganic materials is the effect of Argon incorporation into the material. Incorporation is commonly observed during depth profile experiments especially when the ion beam energy is >100 eV. Previous studies using Raman spectroscopy have shown argon incorporation to affect both the chemical bonding and to induce structural rearrangement of the material [10]. Figure 5 shows a comparison of comparison of Argon 2p and 2s regions for TiO\textsubscript{2} sputtered with 5 kV Ar\textsuperscript{+} and 20 kV Ar\textsubscript{500}\textsuperscript{+}.

After sputtering with monatomic ions, the presence of argon is clearly visible indicating Argon incorporation into the structure of the titania. This is however not the case when using cluster ions (Fig. 6). No Argon was seen when sputtering with 20 kV Ar\textsubscript{500}\textsuperscript{+} clusters. This indicates that all of the Argon leaves the surface into the vacuum after collision with the surface. For 5 kV monatomic argon a steady-state relative atomic concentration of ~2.5 % was reached after having sputtered less than 10 nm into the sample.

4. Conclusions

Here we have shown that the degree of sputter reduction of metal oxides can be greatly reduced using Argon clusters. We believe that the use of massive clusters restricts damage to within the sampling depth of XPS (~6 nm). The damaged material is removed from the surface and enters the vacuum leaving a near pristine surface. Damage is confined to the near surface region leaving the bulk unaffected by the impinging ions. Argon incorporation is also eliminated limiting structural and chemical changes.

5. Acknowledgements

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6. References


