Paper

Reduced Preferential Sputtering of TiO_2 using Massive Argon Clusters

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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 Ar_n^+ 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 Ar_n^+ 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 Ar_n^+ 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 Ar_n^+ 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, Ar_n^+ 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 Ar_n^+ 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]:

$$Y(\varepsilon) = n\varepsilon A\left[1+erf\left(\frac{\varepsilon - U}{s}\right)\right] \qquad (1)$$

where Y, ε, 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 ≈ 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 ≈ 20 eV [3,4]. In simple terms, the Ar_n^+ cluster ion energy per nucleon, ε, must exceed this effective threshold for sputtering to occur. Consequently, Ar_n^+ cluster ion beams of 20 keV n = 500 (ε ~ 40 eV $nucleon^{-1}$) with a 1.25 mm × 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 ε ~ 40 eV $nucleon^{-1}$ should deliver a similar sputtering yield for an organic material using an Ar_n^+ cluster ion beam with only ε ~ 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 ~4 μA and for the Argon clusters ~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 monatomic 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

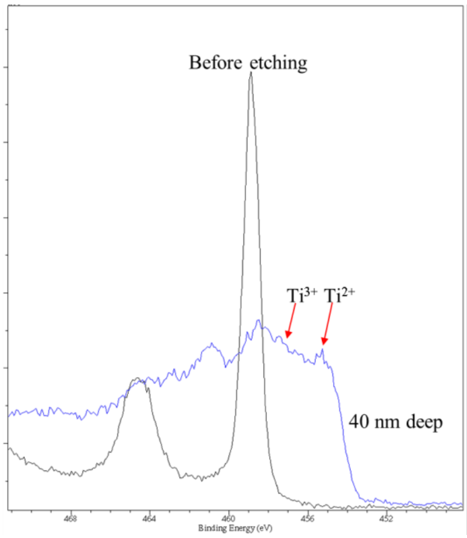

Fig. 1 Ti 2p peak region before (black) and after (blue) sputtering. The TiO_2 thin-film was etched to a depth of 40 nm.

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 characterized 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.

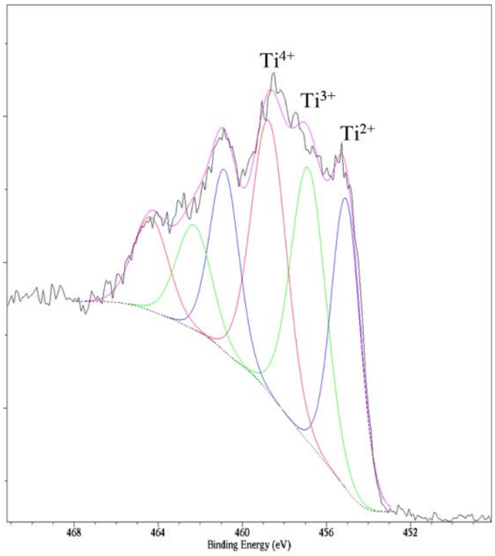

Fig. 2 Peak-fitted Ti 2p region after the thin-film was etched.

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.

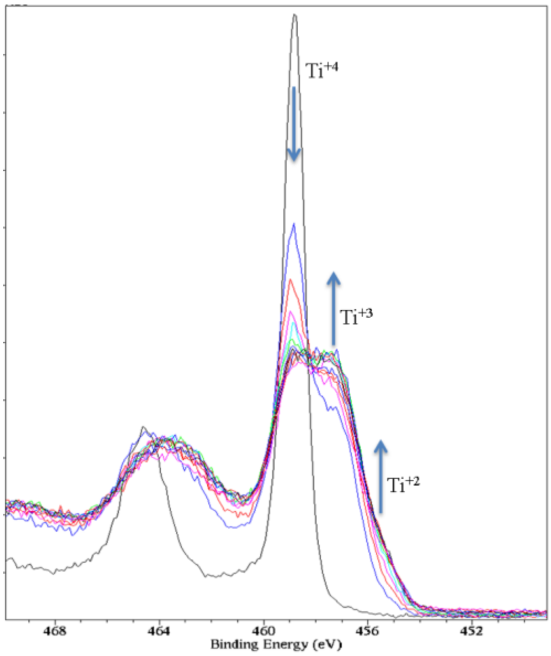

Fig. 3 Ti 2p spectrum when sputtered 20 nm deep using 20 kV $Ar_{500}{}^+$.

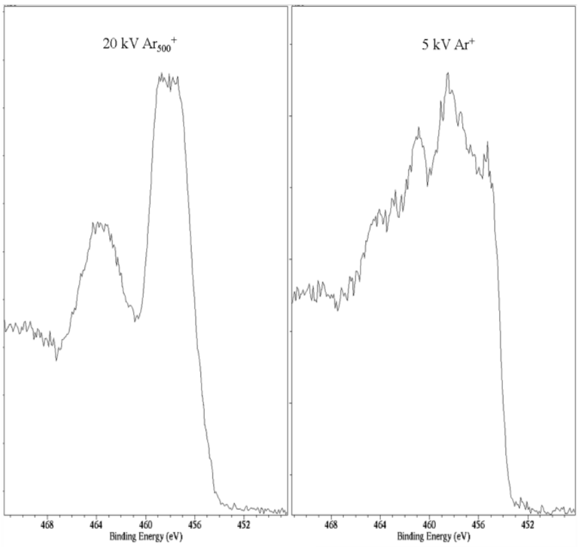

Fig. 4 A comparison of the change in Ti 2p spectrum when sputtered 20 nm using different ion sources.

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 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_{500}^+ 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_2 sputtered with 5 kV Ar^+ and 20 kV Ar_{500}^+.

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_{500}^+ 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.

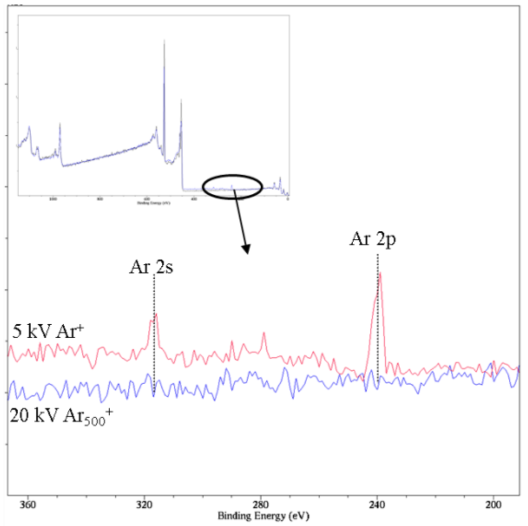

Fig. 5 Comparison of Argon 2p and 2s regions for TiO_2 sputtered with monatomic Argon ions (red) and Argon clusters (blue).

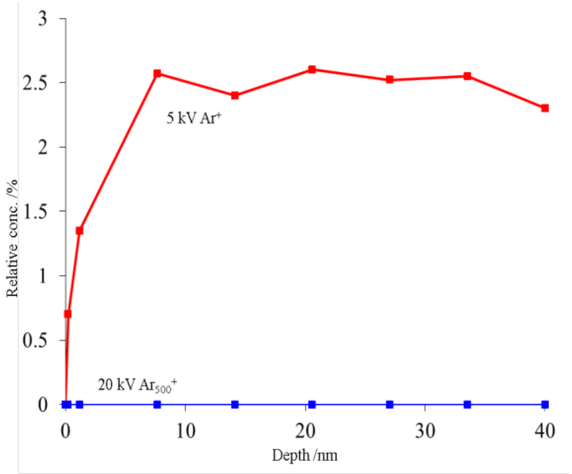

Fig. 6. Argon concentration as a function of sputter depth.

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

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