

## Applications Note

# Reduction in preferential sputtering of TiO<sub>2</sub>

### Overview

Monatomic Ar 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 Ar 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<sub>n</sub><sup>+</sup> clusters as a new methodology for reducing the damaging effects caused by ion bombardment.

### Introduction

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. Until the recent development of Ar<sub>n</sub><sup>+</sup> gas cluster ion sources such depth profile studies have been limited to Ar<sup>+</sup> as the primary ion for sputtering. 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; 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.

### Experimental

Measurements were performed using the state-of-the-art AXIS photoelectron spectrometer and a Gas Cluster Ion Source (GCIS) for sample sputtering using Ar<sub>n</sub><sup>+</sup> cluster ions or monatomic Ar<sup>+</sup>. 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]. The GCIS can deliver Ar<sub>n</sub><sup>+</sup> cluster ions at energies from 1–20 keV and cluster sizes  $n = 250$ –2000. Titania thin-films were prepared via spray-pyrolysis on FTO glass.

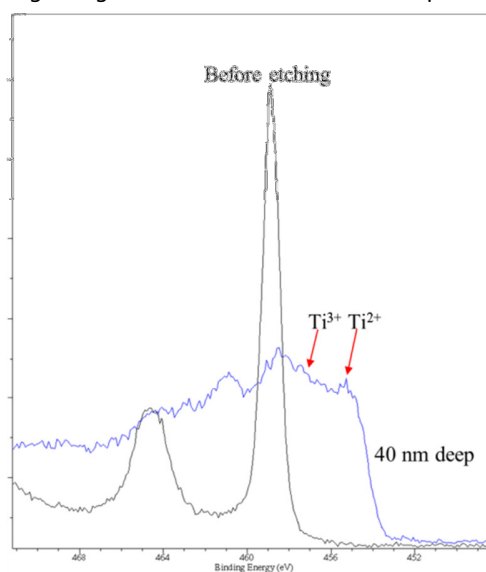
### Discussion

Figure 1 shows the change in structure of the Ti 2p peak before and after sputtering the film to a depth of 40 nm. Monatomic Argon ion bombardment clearly has a significant effect on the chemistry of the thin-film. The change in peak shape has previously been attributed

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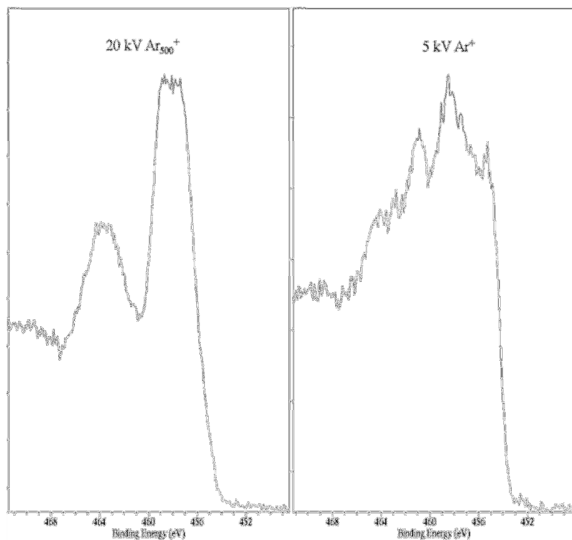
**Keywords:** Titania, GCIS, preferential sputtering, novel materials

to a reduction in the oxidation state of the material from +4 to +3 and +2 states. These reduced states are seen at binding energies of 457.3 eV and 455.7 eV respectively.



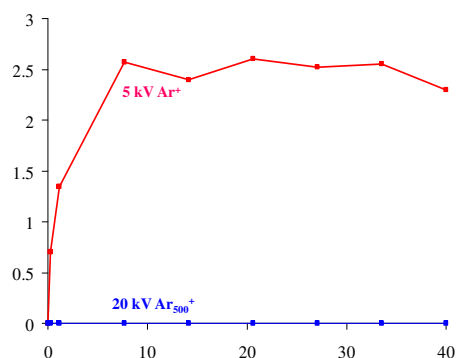
**Figure 1: Ti 2p peak region before (black) and after (blue) sputtering. The TiO<sub>2</sub> thin-film was etched to a depth of 40 nm.**

Having illustrated the damage caused by monatomic Ar<sup>+</sup> ions, 20 kV Ar clusters of  $n=500$  were used for comparison. Figure 2 shows a comparison between the Ti 2p region of the thin-film sputtered 40 nm deep with monatomic Ar<sup>+</sup> and Ar<sub>500</sub><sup>+</sup>. 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.



**Figure 2: A comparison of the change in Ti 2p spectrum when sputtered 40 nm using different ions.**

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 results in a shallower penetration depth, which is restricted to the near surface region. We estimate the penetration depth of the cluster ions to be approximately 6 nm, which is less than the analysis depth of XPS. A shallower 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 >4nm/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 a 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



**Figure 3: Argon incorporation as a function of etch depth using two different sputter ions.**

Argon ions, the etch rate would be so low as to be impractical for all but the most academic of 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 have shown argon incorporation to affect both the chemical bonding and to induce structural rearrangement of the material. Figure 3 shows the level of Argon incorporation as a function of sputter depth for both 5 kV  $Ar^+$  and 20 kV  $Ar_{500}^+$  depth profiles. After sputtering with monatomic ions, the presence of argon is clearly visible. This is however not the case when using cluster ions indicating that all of the Argon leaves the surface into the vacuum after collision with the surface.

## 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 less than the sampling depth of XPS. 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.