The Use of Argon Cluster Ion Sources in Etching of Inorganic Materials with Reduced Chemical Damage: Toward a Better Understanding of Interface Chemistry

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A large fraction of important, common chemical processes take place at the interface between materials. Analytical techniques such as X-Ray Photoelectron Spectroscopy (XPS) [1], Auger Electron Spectroscopy (AES) and Secondary Ion Mass Spectrometry (SIMS) are used to obtain elemental and chemical information from sample surfaces, or the material-vacuum interface. Historically, mono-atomic argon has been used to clean sample surfaces *in-vacuo,* and to cyclically remove sample material then perform an analytical measurement, developing a profile of sample information with depth, often going through multiple layers of material.

All of these surface techniques have specific sensitivity over the same basic depth scale as the differences between bulk and surface properties in most materials, allowing great insight to the chemistry behind processes such as adhesion, corrosion, heterogeneous catalysis, thin film growth, and a wide array of biomaterials applications. Nano-materials add a whole group to the list, as nanoparticles are often small enough in size to have general material properties dominated by surface effects, being made up of nearly all surface. The three main surface analytical techniques all inherently give information on the nano scale, in the direction of observation, independent of the lateral probe size. Coupling this surface specificity with ion etching to remove sample material, then allows the investigation of the chemical structure of samples as a function of depth, with the intent of limiting the damage done to the remaining material. In the ideal situation, the damage layer is completely removed in the etching process.

The use of mono atomic argon to etch inorganic materials dates to the earliest commercial analysis systems. The etching process using mono atomic argon relies on a recoil wave to expel material, leaving the impinging argon atom buried fairly deep in the material, having broken a large number of bonds in the remaining sample above it [2]. The amount of chemical damage being done in this process is often observable in things such as reduction of oxides into mixed sub-oxides, when working on many metal oxides. There is almost always an Argon photoelectron signal in the spectrum taken after any sputtering with mono-atomic argon, due to the embedded atomic argon.

With regard to most all organic materials, mono-atomic argon is generally highly ineffective for use in sputter depth profiling, or cleaning, except in special circumstances. The recoil process described above for inorganic sputtering, fails to eject material in the organic case, rather just scissioning individual bonds, which quickly crosslink, forming a carbonaceous goo that fails to sputter away.

Evidence of the chemical damage done using mono atomic inert gas (Ar) sputter etching is clear in surface analysis data of many metal oxide examples. Figure 1 shows XPS spectra displaying the partial reduction of the sample surface oxide after energetic Ar+ etching. Mono-atomic argon sputtering

efficiency also has great sensitivity on the atomic mass of the sample, leading to preferential sputtering of the lighter elements in materials.

Over the last decade, ions comprising various poly-atomic molecules and clusters have been developed into tools for sputter etching of organic compounds. Certain classes of organic materials were still difficult to etch with the molecular ions, but cluster ions proved hugely successful at imparting all their energy over a wide mass, yielding energies of just a few eV per atom on average. These ionized, argon ice-balls are able to impart this distributed energy in such a way as to essentially remove the entire damage layer, leaving a fresh surface of polymer, or other organic matrix. Unfortunately, while these sources had excellent performance on organic materials, they had difficulty with inorganic materials, which is the exact opposite of the mono-atomic situation.

Additional research has shown that this last observation is not the actual case, and that there are indeed operational regimes that allow these sources to etch inorganic materials. In fact, these sources are being seen to etch inorganic materials with less reduction of the remaining surface oxide, and no argon signal in the sample spectrum.

XPS data from Kratos Axis instruments will be presented, showing that these argon gas cluster ion sources (GCIS) can be optimized to profile metal oxides. Basic comparisons with traditional sputtering are followed with discussion of the effects on sputtering the technologically relevant lead zirconate titanate (PZT), showing the ability to maintain stable etching of these materials, while causing less reduction of the remaining oxide. This work will show how there is still hope that there may be one type of source that is useable across the entire materials range

References:

[1] C Moffitt, Microscopy Today, March (2011) p. 16.
[2] B Garrison, Surface and Interface Analysis, 45 (2013) p. 35.
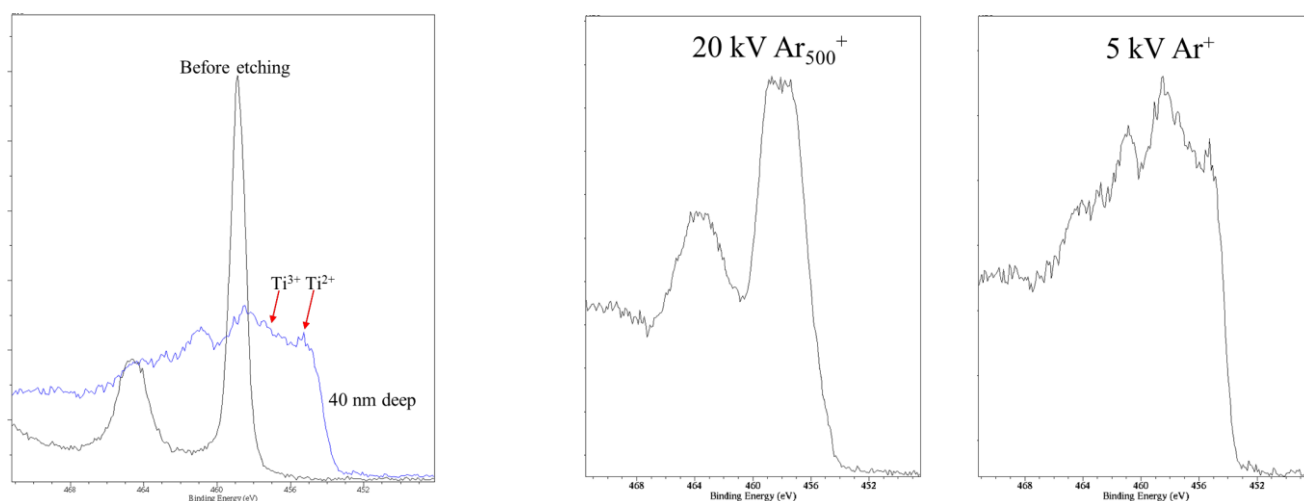
Figure 1. a) Ti 2p photoelectron spectra from a sample before and after sputtering to remove approximately 40nm of material with mono-atomic argon. b) Comparison of the same mono atomic spectrum with the spectrum taken after cluster ion etching to the same depth.